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OKLO NATURAL REACTORS: GEOLOGICAL AND GEOCHEMICAL CONDITIONS - A REVIEW

by

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OKLO NATURAL REACTORS: GEOLOGICAL AND GEOCHEMICAL CONDITIONS - A REVIEW

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ABSTRACT

Published as well as unpublished material on the Oklo natural reactors in Gabon was evaluated with regard to the long-term aspects of nuclear waste disposal. Even though the vast data base available at present can provide only a site specific description of the phenomenon, already this material gives relevant information on plutonium retention, metamictization, fission product release, hydrogeochemical stability and migration of fission products. Generalized conclusions applicable to other nuclear waste repository sites would require the quantitative reconstruction of the coupled thermo-hydrologic-chemical processes. This could be achieved by studying the deviations in the $^{2}H/^{1}H$ and $^{18}O/^{16}O$ ratios of minerals at Oklo. A further generalization of the findings from Oklo could be realized by examining the newly-discovered reactor zone 10, which was active under very different thermal conditions than the other reactors.

RÉSUMÉ

La documentation publiée ou non sur les «réacteurs naturels» d'Oklo au Gabon a été évaluée quant aux aspects à long terme de l'évacuation des déchets nucléaires. Même si l'importante base de données qui existe actuellement peut donner seulement une description du phénomène par rapport à un site précis, cette documentation fournit déjà de l'information pertinente sur la rétention du plutonium, la métamictisation, la libération de produits de fission, la stabilité hydrogéochimique et la migration des produits de fission. Des conclusions généralisées applicables à d'autres sites de dépôt des déchets nucléaires exigeraient la reconstitution quantitative de l'ensemble des processus thermique, hydrogéologique et chimique, ce que l'on peut faire en examinant les écarts des rapports $^{2}H/^{1}H$ et $^{18}O/^{16}O$ dans les minéraux d'Oklo. Il serait possible de généraliser davantage les résultats des recherches grâce à l'examen du «réacteur naturel» n° 10 qui a été récemment découvert et qui était en activité sous des conditions thermiques très différentes de celles des autres «réacteurs naturels».

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1. INTRODUCTION

In 1972, French scientists at the Pierrelatte Diffusion Plant found an isotope anomaly in the uranium ore originating from the Oklo repository in Gabon, Africa. The ^{235}U content of the ore averaged 0.62% as compared to the normal ^{235}U content of 0.7202%. The investigation of the other elements in the depleted uranium zones also showed unexpected anomalies. There were abnormal isotopic abundances found of the stable end-elements or members of the decay series from the fission-product region grouped around the ^{235}U thermal fission yield curve. As the ore composition resembled nuclear fuel of slight burnup after decay of the fission products, the scientists concluded that Oklo is a fossile fission reactor. During later investigations, spots of ^{235}U enrichment within the zones of nuclear reaction were also found indicating that sporadically even breeding conditions must have existed. Subsequent research confirmed this conclusion and already before 1975 (the first IAEA meeting on Oklo), the theory was generally accepted. Further research followed under the auspices of an IAEA advisory group. Later this was changed into a technical working group which organized the second meeting on Oklo in 1977. At that time a new aspect of the Oklo phenomenon received attention. Oklo was looked upon as a naturally created experiment in geologic disposal of irradiated nuclear fuel.

The purpose of this review is to summarize the information on the precambrian nuclear fission reactions which occurred at Oklo, to determine the present status of knowledge about this phenomenon and to direct research at areas relevant to long-term nuclear waste management.

The annotated bibliography is divided into sections on Geology and Tectonics, Petrology and Mineralogy, Nuclear Geologic Parameters and Migration/Retention. The critical summaries are presented chronologically according to subject matter. If there was no reason to do otherwise we discussed related articles together. The information for this review was obtained from two major symposia on Oklo, various journals, books, proceedings, scientific reports, abstracting services and private material. We made an effort to include the latest results. All summaries were prepared by us. The abstracting was divided between the two authors. Assignment of papers for discussion was based on the expertise of the author: articles under sections Geology, Tectonics, Petrology and Mineralogy were reviewed by W. Church and those under Nuclear Geochemistry and Migration/Retention by A.T. Jakubick. Valuable help was given to us by F. Weber and F. Gauthier-Lafaye of University of Strassbourg and substantial new material provided by D. Curtis of Los Alamos National Laboratory.

2. ANNOTATED BIBLIOGRAPHY

2.1 Geology and Tectonics

2.1.1 Regional Setting

Azzibrouk Azziley, G. 1982. Lithostratigraphie-microtectonique et metamorphisme de la vallee de l'Ogoue entre NDjole et Booue, Gabon. Memoire de D.E.S., Universite de Nancy, 51 p.

Cortial, F. 1985. Les Bitumes du Francevillien (Proterozoique Inferieur du Gabon, (2000 Ma) et leurs kerogenes; relations avec les mineralisations uranifere. These, Docteur de l'Universite, Universite de Strasbourg, 183 p. (p. 13).

Curtis, D.B. and Gancarz, A.J. 1983. Radiolysis in nature: evidence from the Oklo natural reactors. SKBF/KBS 83-10, 55 p. (Fig. 1).

Gauthier-Lafaye, F. and Weber, F. 1981. Les concentrations uraniferes du Francevillien du Gabon: leur association avec des gites a hydrocarbures fossiles du Proterozoique inferieur. C.R.Acad. Sc. Paris, t. 292, Ser.II, no.1, 69-74.

Weber, F. and Gauthier-Lafaye, F. 1981. Etude geologique du trace du chemin de fer transgabbonais. Troncon de Lastourville a Bongo-Badouma. Rapport ULP-GAUFF, 160 p.

Molina, P. and Besombes, J.C. 1975. Place du Francevillien dans le contexte geologique de l'Afrique. Le phenomene d'Oklo - The Oklo phenomenon, Int. At. En. Agency, Vienna, p. 3-15.

The Francevillien basin is located in the southeast part of the Republic of Gabon. It is limited to the north and south by the Archean age crystalline massifs of North Gabon and Chaillu, respectively. To the west the basin is bordered by the metamorphic rocks of the Ogooue system and to the east by horizontal Mesozoic continental deposits of the Stanley-Pool and Batekes Plateau successions.

The Francevillien basin, which covers an area of about 30 000 square kilometers, is divisible into a number of smaller basins : the Lastourville basin to the west, the Okondja to the north, and the Franceville to the south. The basin can be divided into four NW-SE decakilometric structural zones which can be further divided into a number of kilometer sized fold belts (Gauthier-Lafaye 1977, Fig. 2).

The rocks of the southern Franceville basin, which forms an elliptical northwest-southeast elongated depression covering an area of about 2 500 square kilometers, is essentially composed of arenites, mudstone, and felsic volcanogenic material of Lower Proterozoic age. The uranium deposits and natural reactors of Oklo are all located within the basal sandstone-conglomerate unit of the Francevillien succession of the Mounanan-Moanda fold belt of the Ogooue structural zone (Gauthier-Lafaye 1977, p. 1).

The metamorphic rocks of the Ogooue mobile belt, considered to be equivalents of the Francevillien, have undergone polyphase deformation involving three events (Azzibrouk Azziley, 1982). The first two events, which were coeval with a phase of greenschist to amphibolite grade metamorphism involving the development of a penetrative foliation, culminated with the emplacement of a suite of pegmatites at about 1.98 Ga. The third event at about 1.87 Ga involved the construction of a first-order N-S trending anticlinorial structure. Schistosity associated with the latter structure occurs only on a local scale.

2.1.2 Stratigraphy

Cortial, F. 1985. Les Bitumes du Francevillien (Proterozoique Inferieur du Gabon, (2000 Ma) et leurs kerogenes; relations avec les mineralisations uranifere. These, Docteur de l'Universite, Universite de Strasbourg, 183 p. (p. 19-28).

Gauthier-Lafaye, F. 1979. Controle geologique de l'exploitation des zones de reaction 7-8 et 9, Oklo - Gabon. Institut de Geologie, Universite Louis Pasteur, Strasbourg (manuscript).

Gauthier-Lafaye, F. 1977. Oklo et les gisements d'uranium du Francevillien: aspects tectoniques et metallogenique. These 3eme cycle, Strasbourg, 92p.

Gauthier-Lafaye, F. and Weber, F. 1981. Les concentrations uraniferes du Francevillien du Gabon: leur association avec des gites a hydrocarbures fossiles du Proterozoique inferieur. C.R. Acad. Sc. Paris, T. 292, Ser. II, No. 1, 69-74.

Gauthier-Lafaye, F. and Weber, F. 1984. Effets de deformations posterieures a une diagenese siliceuse d'enfouissement sir le comportement microthermometrique des inclusions fluides: cas du reservoir greseux uranifere du Francevillien (Gabon). C.R. Acad. Sc. Paris., t. 299, Serie II, No. 9, p. 555-560.

Leclerc, J. and Weber, F. 1977. Geology and genesis of the Mouanda manganese deposits. Republic of Gabon. 25th Intern. Geol. Congress Symposium, Geology and Geochemistry of Manganese, v.104, no.3.

Weber, F. 1968. Une serie precambrienne du Gabon: Le Francevillien, sedimentologie, geochimie. Relation avec les gites mineraux associes. Mem. Serv. Carte Geol. Als. Lorr., v. 28, 328 p.

The Francevillien is divided into 5 formations (Weber, 1968; Leclerc and Weber, 1977; Cortial, 1985, Figs. 2, 4), from the base upwards:

1) a sandstone-conglomerate sequence - FA.

2) a dominantly mudstone sequence - FB; divided into a lower part (FB1) with mudstones, carbonaceous black shales, and manganiferous, ferriferous, and dolomitic pelites, and rare tuffa-

ceous horizons, and an upper part (FB2) composed of an upward fining cycle of sandstones and carbonaceous shales.

3) a unit of chert, carbonaceous shale, dolomite and tuffaceous material - FC.

4) a carbonaceous shale unit containing a progressively greater amount of tuffaceous material towards its top - FD.

5) a tuffaceous sequence of intercalated sandstones, shales, carbonaceous shales and carbonate.

The FA succession of the Francevillien is composed of a thick (1000 m) formation of generally upward fining sandstone and conglomerate formed in a fluviatile environment (braided stream). Conglomerates of the lower part of the FA sequence are relatively enriched in thorium. However, in the internal zones of the basin, the sandstones are finer and thicker, and in the upper part of the formation are intercalated with black mudstones charged with organic (algal) material, a facies representative of marine intertidal conditions.

The sandstones are composed of quartz, feldspar (mostly microcline), micas, and chloritized material. The phyllitic minerals are oriented parallel to bedding. Heavy mineral concentrations commonly associated with thin conglomeratic units of the sandstone of the lower part of the succession include zircon, monazite, and apatite. Coarser sandstones and conglomerates contain a higher proportion of chlorite relative to 1 Md illite as clay matrix material. Upwards in the FA succession, chlorite/illite matrix material tends to be replaced by cement of carbonate (dolomite) and gypsum/anhydrite composition, and, in the upper 150 metres of the succession, by quartz overgrowths. Detrital elements in the uppermost part of FA are also more mature, plagioclase is rare, and opaque minerals are disseminated in the matrix and microfractures. The upper part of the FA succession is considered to be deltaic in origin (Cortial, 1985, p. 20).

Mudstones of the lower part of the FB succession change colour progressively upwards from green to grey to black. The black coloured unit is composed of alternating beds of calcareous silts and micaceous pelitic rocks enriched in carbon. The mudstones are overlain by a middle sequence (FB1b) of sandy mudstones which in places (Oklo) is represented by conglomeratic sandstones and dolomitic debris flows which channel the underlying mudstones. This succession is overlain by black shales (FB1c) with horizons of dolomitic, ferruginous, phosphatic and manganiferous material. In its upper part the black shale unit becomes more sandy and grades into the sandstones of the sandstone - shale regressive cycle of the FB2a - FB2b units, respectively.

Although the FB mudstones are widely distributed in the Francevillien basin, at the basin margins the upward fining FA - FB1a cycle was interrupted by the deposition of a relatively immature facies composed of channel sands; the latter in places being separated from the underlying FA pelitic rocks by an angular unconformity. This would suggest that the development of the Franceville basin at that time was

interrupted by a phase of crustal readjustment prior to an acceleration in basinal downwarping and the deposition of the black shales and cherts of units FC and FD.

2.1.2.1 Diagenesis (Gauthier-Lafaye 1977, p. 5; Cortial, 1985, p. 18)

Other than the conversion of clay to illite and the formation of primary quartz overgrowths, early diagenesis involved the alteration of plagioclase to quartz, sericite and chlorite, the incorporation of hydrocarbons along cleavage and fractures in plagioclase, and the alteration of biotite involving chloritization and epitaxial overgrowth of muscovite. Relative to the latter diagenetic transformations the carbonate diagenesis noted in the sandstones of the middle part of the FA succession appears to be late. Hydrocarbons were mobile both prior to and after the phase of formation of quartz overgrowths, whereas sulphides are essentially localised within fractures and are therefore late, introduced after the development of a secondary porosity. Oxides in the sandstones are iron oxides, the presence of which gives a red colour to the sandstones of the central part of the Franceville basin. The illites in sandstones of the FA succession are generally of 1M type, 2M illites only being recognised in sandstones of the deepest part of the basin.

Estimates of temperature during diagenesis, based on a study of fluid inclusions in quartz overgrowths and calcite hydraulic fracture fillings, are according to the Gauthier-Lafaye and Weber (1984) only reliable for the late stage of diagenesis related to orogenic deformation and the precipitation of carbonate. They estimated a minimum temperature of 140-160 degrees C at a depth of 2500-5000 m for the diagenetic phase which gave rise to the carbonate, pyrite, pitchblende paragenesis. Gauthier-Lafaye and Weber (1984) consider the dolomitic cement found in some sandstones to have been precipitated over a long period of time.

2.1.2.2 Uraniferous Zones

(Gauthier-Lafaye, 1977, p. 8; Fig. 8, 11, 12; Gauthier-Lafaye, 1979; Gauthier-Lafaye and Weber, 1981).

In the Franceville basin there are two uraniferous zones of unequal economic importance : the exploited Mounana - Oklo zone, and the presently unexploited Franceville zone (Mikouloungo deposit). The latter deposit is localized preferentially in sandstones of FA along a fault contact with overlying FB mudstones whereas the Mounouna deposit is located within immature FA sandstones below the unconformably overlying FB deposits. Uranium and also vanadium are preferentially enriched in fault zones. Pitchblende in the sandstones is generally included in phyllitic phases of the sandstone matrix, commonly in association with bitumens and sulphides, and even barite. At Oklo most of the uranium deposits are located in the uppermost "C1" sandstone unit of the FA succession (Gauthier-Lafaye, 1977, Fig. 12). (Uranium is also

concentrated in another sandstone unit ("C2") where it is involved in the pinched synform present to the north of Oklo). Typically the uranium in the 'C1' sandstones is found in the form of pitchblende (.4-.6% UO_2; rarely more than 1%) in highly silicified black sandstone (Gauthier-Lafaye, 1977, p. 17). The ore is invariably associated with hydrocarbon material and, more rarely, with calcite. In a second type of ore the uranium (5 to 25% UO2) is distributed around hematite spots from which it is separated by a fringe of discoloured material representing a small scale oxy-reduction front. This type of ore is found in zones of strong tectonic disturbance, the uranium occupying micro-shear planes in quartz (Gauthier Lafaye, 1977).

2.1.3 Hydrocarbons

Cortial, F. 1985. Les bitumes du Francevillien (Proterozoique Inferieur du Gabon, (2 000Ma.) et leurs kerogenes relations avec les mineralisations uranifere. These, Docteur de L'Universite, 161p.

Vandenbrouke, M., Rouzaud, J.N., Oberlin, A. 1978. Etude geochimique de la matiere organique insoluble (kerogene) du minerai uranifere d'Oklo et de schistes apparente du Francevillien (I. A. E. A.-TC-119/10). Natural Fission Reactors, Proc. Tech. Comm. Meet, Paris 1977. Panel Proceedings Series, I. A. E. A., Vienna, p. 307-352. (ISBN 92-0-051078-7)

Alpern, B. 1978. Etude petrographique de la matiere organique d'Oklo (I. A. E. A.-TC-119/11). Natural Fission Reactors, Proc. Tech. Comm. Meet, Paris 1977. Panel Proceedings Series, I. A. E. A., Vienna, p. 333-352. (ISBN 92-0-051078-7)

Rouzaud, J.N., Oberlin, A., Vandebroucke, M. 1978. La microscopie electronique comme moyen d'analyse et de caracterisation; application aux substances organiques provenant de l'environnement du reacteur naturel d'Oklo (Gabon). Soc. Geol. Fr. Bull., v. 20, no. 5. (supplement), p. 238-241.

Cassou, A.-M., et al. 1975. Etudes chimiques et observations microscopiques de la matiere organique de quelques mineralisations uraniferes. Le phenomene d'Oklo - The Oklo phenomenon, Int. At. En. Agency, Vienna, p. 195-206.

The hydrocarbon content of the FB mudstones lies between 5 and 8% (up to 20%) whereas the FA quartzites generally contain less than 0.2% (Cortial, 1985, p. 162) but with some values as high as 1.53% Vandenbrouke et al., 1977). The FB mudstones concentrate Cu, Ni, Co, Zn, and V, but generally have low concentration of U. In the FA sandstones, bitumens located in primary pores in silicified zones are only slightly oxidized, are sterile in U, and are as enriched in V as the FB mudstones. Uranium enrichment occurs in association with highly oxidized (anthracitic) bituminous material occupying fractures (secondary porosity). In this case bituminous material is impoverished in vanadium, supposedly displaced by the oxygenic solutions depositing the uranium. In places the vanadium is sufficiently concentrated to

merit exploitation (Mounouna). In sandstones with low uranium concentrations the uranium was precipitated within and at the borders of the hydrocarbon material, within which it is also present in the form of urano-organic complexes. In view of the oxidized yet poorly oriented nature of the bituminous material, the complexing and oxydation would seem to have taken place while the hydrocarbons were still plastic.

There is no correlation between uranium concentration and amount of organic carbon, the degree of uranium enrichment seems to be related to the intensity of development of secondary porosity associated with tectonic movements. Uranium grades of 5 to 25% occur in rocks which have undergone little silicification but which have suffered strong post diagenesis intra-bed shearing. The highest uranium concentrations of 20-30% are associated with fault breccia zones and the generation of an even higher degree of secondary porosity (Cortial, 1985).

2.1.4 Structure

Gauthier-Lafaye, F. and Weber, F. 1984. Effets des deformations posterieur a une diagenese siliceuse d'enfouissement sur le comportement microthermometrique des inclusions fluides: cas du reserervoir greseux uranifere du Francevillien (Gabon). C.R. Ac.Sc., t.299, SerII, no.9,555-560.

Ruhland, M. 1982. Examples d'organization des reseaux de fractures mineralises dans divers models structuraux. Vein-type and similar uranium deposits in rocks younger than Proterozoic; Tech comm Meet, Int. At. En. Ag., Vienna, Austria, p. 47-61.

Gauthier-Lafaye, F. 1977. Oklo et les gisements d'uranium du Francevillien: aspects tectoniques et metallogenique. These 3eme cycle, Strassbourg, 92p.

Gauthier-Lafaye, F., Ruhland, M., Weber, F. 1975. Analyse tectonique du gisementd'Oklo. Le phenomene d'Oklo - The Oklo phenomenon, Int. At. En. Agency, Vienna, p. 103-118.

The most comprehensive discussion of the structure of the Francevillien, and more specifically the Oklo reactor zone, is provided by Gauthier-Lafaye (1977).

The Francevillien basin is divided into two structural domains by the sinistral N20 degree striking Matsatsa fault. To the northwest of the fault the Francevillien is relatively little deformed, whereas to the southeast the area occupied by the Franceville and Okondja basins is cut by an important series of dextral wrench faults striking N140 and North to N340 degrees. The maximum principal stress of the stress system responsible for the faulting is directed 10 degrees west of North (Gauthier Lafaye, 1977).

The faults were active during, as well as following, sedimentation, and have exerted an important control on the compartmentalization of the

Francevillien into separate basins. Subsidence concomitant with sedimentation provoked the formation of NW-SE to E-W oriented distentional faults which divided the basin into a number of multi-kilometre sized fault-bounded structural blocks. Depth of subsidence is estimated to be of the order of 3000 to 5000 m. During subsequent uplift, the sandstones in particular underwent non-penetrative shear deformation. The fault system affecting the Franceville has evidently exerted an important control on the uranium mineralization - particularly evident in the case of the Mikouloungo deposit (Gauthier-Lafaye, 1977, Fig. 8). In the case of the Mounana - Oklo belt, faulting is also considered to reflect the presence of a major basement fracture. Where faults interfere, as at Mounana, deformation is intensified. In this case the dextral fault is related to a phase of brittle deformation whereas the complemetary sinistral fault involved the development of folds.

2.1.5 Radiometric Ages

Gancarz, A., Cowan, G., Curtis, D., and Maeck, W. 1980. 99Tc, Pb and Ru migration around the Oklo natural fission reactors, in Northrup, C.J.M. Jr., Scientific Basis for Nuclear Waste Management, v. 2, p. 601-608.

Bonhomme, M.G. and Weber, F. 1978. Francevillien revisited; radiochronology of a fossil nuclear reactor environment. Short Papers of the 4th International Conference, Geochronology, Cosmochronology, Isotope Geology, 1978; US Geol. Surv., Open-File report no. 78-701, p. 47-48.

Bonhomme, M., Leclerc, J. and Weber, F. 1978. Etude radiochronologique complementaire de la serie du Francevillien et de son environnement (I. A. E. A.-TC-119/6). Natural Fission Reactors, Proc. Tech. Comm. Meet, Paris 1977. Panel Proceedings Series, I. A. E. A., Vienna, p. 19-24. (ISBN 92-0-051078-7)

Gancarz, A.J. 1978. U-Pb age (2.05e+9 years) of the Oklo uranium deposit (I.A.E.A.-TC-119/40). Natural Fission Reactors, Proc. Tech. Comm. Meet, Paris, 1977. Panel Proceedings Series, I.A.E.A., Vienna, p. 513-520.

Maeck, W.J., Apt, K.E., and Cowan, G.A. 1978. A possible uranium-rethenium method for the measurement of ore age (I.A.E.A.-TC-119/32). Natural Fission Reactors, Proc. Tech. Comm. Meet, Paris, 1977. Panel Proceedings Series, I.A.E.A., Vienna, p. 535-542.

Lancelot, J.R., Vitrac, A., and Allegre, C.J. 1975. The Oklo natural reactor; age and evolution studies by U-Pb and Rb-Sr systematics. Earth Planetary Sci. Letters, v. 25, No. 2, p. 189-196.

Weber, F. and Bonhomme, M. 1975. Donnees radiochronologiques nouvelles sur le Francevillien et son environment. Le phenomene d'Oklo - The Oklo phenomenon, Int. At. En. Agency, Vienna, p. 17-35.

Devillers, C., Ruffenach, J.-C., Menes, J., Lucas, M., Hagemann, R., et Nief, G. 1975. Age de la mineralisations de l'uranium et date de la

reaction nucleaire. Le phenomene d'Oklo - The Oklo phenomenon, Int. At. Eng. Agency, Vienna, p. 293-302.

Hagemann, R., et al. 1975. Estimation de la duree de la reaction; limitations imposees par les donnees neutroniques. Le phenomene d'Oklo - The Oklo phenomenon, Int. At. En. Agency, Vienna, p. 415-423.

Hagemann, R., Lucas, M., Nief, G., Roth, E. 1974. Mesures isotopiques du rubidium et du strontium et essais de mesure de l'age de la mineralisation de l'uranium du reacteur naturel fossile d'Oklo. Earth Plan Sci. Lett, v. 23, No. 2, p. 170-176.

Loubet, M. 1974. Caracteristique et age du reacteur naturel (d'Oklo) etudiee a l'aide de l'analyse des terres rares. Reun. Annu. Sci. Terre, no.2, p. 266.

The generally assumed age of 2.14 +/-.143 Ga or greater than 2.14 Ga for the Francevillien is based on the Rb/Sr radiometric age of the N'Goutou syenitic complex (Bonhomme and Weber, 1978). The age relationship of the syenite to the Francevillien is nevertheless uncertain, as is also the age of the initial introduction of uranium. The age of the event involving uranium secondary enrichment is however estimated to be about 2.05 +/-.06 Ga on the basis of a U-Pb study of uranium rich ore (Gancarz, 1978). This date is close to the 1.98 +/-30 Ga age of the pegmatite suite intrusive into the supposed Francevillien rocks of the Ogooe complex. The pelitic rocks of the Francevillien became isotopically closed at about 1.87 Ga, perhaps coeval with the anticlinorial erection of the Ogooe complex. However, in the vicinity of the Oklo reaction zones, Rb and Sr isotopes continued to undergo isotopic homogenization until about 1.7 Ga. The reactor age may most closely be represented by the Rb/Sr age of coarse illite (sample 922; 1.947 Ga.) in some units of the FA sequence beyond the reactor zone, as well as in the K/Ar age of coarse illite (sample A 1245; 1.945 Ga.) in the reactor environment.

Younger events involve the intrusion of a suite of diabase dikes about 0.97 Ga (Bonhomme, Leclerc, and Weber, 1978). The lower intercept of a concordia plot indicates a possible event at about 300 Ma (Devillers et al. 1975). However, the lower intercept on concordia plots may equally be explained in terms of continuous lead diffusion rather than episodic lead loss, and this apparent 'event' may have no significance. It does however indicate that a mobile phase has been present throughout the history of the uranium bearing rocks.

2.1.6 The Natural Reactors

Wright, R.J. and Rautman, C.A. 1980. Grants and World Uranium. Geology and mineral technology of the Grants Uranium Region 1979, Memoir - New Mexico Bureau of Mines and Mineral Resources, no. 38, p. 22-35.

Gauthier-Lafaye, F. et al. 1980. Le gisement d'Oklo et ses reacteurs de fission naturels. Proceedings of the International Uranium Symposium on the Pine Creek Geosyncline, I.A.E.A. Proc. Ser. (III), no. STO/PUB/555,

p. 663-673.

Norris, A.E. 1980. Oklo natural fission reactor program; October 1 - December 31, 1979. . Los Alamos Science Lab, Rep., No. LA-8281-PR, 6pp.

Norris, A.E. 1980. Oklo natural fission reactor program; July 1 - September 30, 1979. . Los Alamos Science Lab, Rep., No. LA-8189-PR, 6pp.

Branche, G. 1979. Les reacteurs de fission naturels d'Oklo. DtsGeol. Ges., Z., v. 130, no., 2, p. 641-658.

Gauthier-Lafaye, F. 1979. Controle geologique de l'exploitation des zones de reaction7-8 et 9 Oklo - Gabon. (manuscript).

Naudet, R. 1979. Nouvel examen des problemes poses par les zones de reactions 7-8. (manuscript).

Bouska, V. 1978. An ancient natural uranium reactor. Geol. Pruzkum, v. 20, no. 4, p. 121.

Brookins, D.G. 1978. Uranium deposits and spent fuel rods. Annual Meeting, Geological Society of America Abstracts with programs, v. 10, no. 7, p. 372.

Brookins, D.G. 1978. In Paris, Oklo reactor re-analysed. Geotimes, v. 23, no. 3, p. 27-28.

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The natural reactors at Oklo for which information is currently available form two zones numbered 1 to 6 and 7 to 9, respectively. While separate and distinct features, they are all located within an uranium-enriched (5-20% UO_2) hematite-bearing horizon (bed 'C1') representing the uppermost unit of the FA sandstone succession at Oklo. Reactors 1-6 are located over an outcrop distance of 140 metres around the hinge zone of an open fold plunging in a direction N50, whereas reactors 7-9 (Gauthier-Lafaye, 1979) are located at the point of intersection of unit 'C1' with a local kink band in the underlying sandstones and occupy a surface distance of 30 metres (Gauthier-Lafaye,

1977, Fig. 26; Tchibena Makosso, 1982, Fig. 6). Reactors 1 to 6 are disposed within bed 'C1' such that the reactors are located on progressively lower structure contours in the order 1, 2, 5-6, and 3-4.

The location of the reactors can be related to the presence of local fault and fold structures in underlying units, the Oklo reactors occurring in a zone delimited by faults oriented N and N140 (Gauthier-Lafaye, 1977, p. 22; Fig. 9, 13).

In general the reactor zones are concordant with the stratification, are between .2 and 3 metres wide measured normal to the stratigraphic plane and 15 to 20 metres long measured within the plane, and occupy a volume of the order of a few hundred cubic metres. Within the reactor zones, however, the geometry of the core is not necessarily concordant with that of the enveloping stratigraphic units (Gauthier-Lafaye, 1979, Fig. 27). The reactors are invariably located within zones of brecciation involving hematite spotted sandstones that have undergone little silicification and which usually exhibit a fairly stong degree of shear deformation.

The reactor cores are invariably surrounded by a series of mineralogically zoned aureoles of argillitic material, which extend outwards for a distance of about two metres. As a result of the nuclear reactions in the core, the surrounding country rock sandstones have commonly been converted by a process of desilication to rocks of argillitic composition. The transformation involved substantial loss of rock material and consequent thinning of unit 'C1', as a result of which the overlying FB sedimentary rocks commonly down drape into the void created as a result of the loss in mass. The down draped zones are often associated with the presence of a major fracture and are lined by a grey plastic clay. Where 'corrosion' of the 'C1' sandstones has taken place, however, the down draped FB rocks are not in all cases separated from the sandstones by reactor zone argillites (e.g. Gauthier-Lafaye, 1979, Fig. 8).

Compared with zone 1-6, the reactors of zone 7-9, while also located within bed 'C1', are smaller and contain a particularly high concentration of hydrocarbon material. The latter, however, is less evolved, and has a lower concentration of uranium. The uranium in reactor zones 7-9 is also dispersed rather than present as large crystals. In some large masses of hydrocarbon material, uraninite may be exclusively enclosed in concentrations as high as 35%. The latter feature implies that fission took place in situ within the bituminous material.

2.2 Petrology

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The reactor zones comprise a core and two outer aureoles. The outer aureole is characterized by the presence of 2M illite (illite in the country rock is 1M illite), and the intermediate aureole by the presence of magnesian chlorite (chlorite of the country rock is iron rich). Where the rocks surrounding the reactor zone argillites are sandstones, quartz grains in the latter show signs of desilication and M2 illites may be present to a distance of more than a 15 cm beyond the argillite-sandstone boundary. Where the surrounding rocks are pelitic, the transformation of country rock to reactor zone argillite is more transitional. Again, however, M2 illite makes it first appearance in the surrounding country rocks more than a metre beyond the boundary of disappearance of quartz by dissolution. The M2 illites in the reactor zone are disoriented whereas phyllitic minerals in the sediments are oriented.

Quartz is hardly ever found in the inner aureole and core zones; where found it is enriched in uranium. Zircon also tends to be absent from the core, their former presence being marked however by pseudomorphs of illite and hematite. Leucoxene and sulphide minerals (galena and pyrite) are common as fracture fillings and dispersed grains in the core, whereas hematite is sometimes common as globular or elongated fibrous networks surrounding uraninite and separated from it by a narrow rim (100 microns) of illite with some goethite. Hematite is however absent from the aureole rocks. Whereas the aureole may contain both uraninite and pitchblende, the innermost core zone is marked by the presence of uraninite only. The core also has a greater concentration of chlorite.

Fission products, although present in uraninite of the core zone, are absent from the core zone gangue and the surrounding aureole, and it is assumed that fission products that were accepted into solution were removed completely from the reactor zone and in part redeposited in country rocks beyond the M2 illite aureole. Anomalous 235-uranium values may however be found in the aureole suggesting that some slight amount of 235-uranium was transported into the aureole. Curtis and Gancarz (1983) suggest that such mobility is a consequence of the radiolytic breakdown of water during the nuclear reaction.

According to Tchibena Makoso (1982) the phyllitic minerals of the reactor zone are more homogeneous in composition than those of the country rock sediments. Towards the core, the chloritic minerals of the aureole become less magnesian and more aluminous and siliceous, whereas the sericitic minerals become richer in iron, magnesium, and sodium, and depleted in potassium. Late stage crystallization of phyllitic minerals as fracture fillings involved the formation of a sericite close to true muscovite in composition, and an iron-rich chlorite compositionally similar to that found in the matrix of the normal sediments outside the reactor zone. Commensurate with changes in mineralogy the core rocks are, according to Curtis and Gancarz (1983), relative to alumina, enriched in ferrous iron and calcium, and have a higher ferrous to ferric ratio. However, according to the mass balance calculations of Tchibena-Makosso (1982), compared to an Al/Fe ratio of 3-4 for unaltered country rock, material of the aureoles with a UO_2 concentration of about 4 kg/dm^2 have an Al/Fe ratio of 1.7, and are relatively enriched in K,

Al, Mg, Fe, and Ti and depleted in Si, whereas the K depleted core zone with the highest U values have an Al/Fe ratio of 1.4. It might also be remarked that there is a marked correlation between U, Pb, Ca, and Mn, between K and B, and between high uraninite and the Fe content of chlorite. There is also an absence of fission products in the core zone argillaceous material.

2.2.1 Reactor Zone Uranium

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Uranium in the reactor core is present only in the form of tetravalent uraninite, whereas in the aureole uranium occurs both as uraninite and pitchblende. Individual grains of uraninite contain high concentrations of fission products and preserve the effects of radiation damage. The ratio of 235 uranium to 238 uranium varies from sample to sample. However, small pieces of uraninite and single grains are homogeneous in terms of their isotopic composition. It is not established whether the uraninite is stoichiometric or not.

2.2.2 Temperatures During Fission

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Vidale (1978) claimed the presence of brown pleochroic biotite in zones 2 and 5 and up to 4m outside limits of zone 2, indicating temperatures greater than 400C. Fine grained muscovite is rimmed by biotite and chlorite as well as vice versa. Vidale also indicated that sillimanite pseudomorphs, composed of chlorite or kaolin, are recognisable in the reactor zone, as well as fresh fibrolite in a fragment (sample #2282) occurring with a mixture of different metamorphic rock types in one of the breccia bodies. The presence of sillimanite indicates a reactor temperature of 650°C.

Detrital biotite present in the country rocks is altered and disappears as the reaction zones is approached; the new biotite of the reactor zone gets coarser towards the interior of the zone. Vidale also noted the presence of globular features resembling immiscible melt structure in zone 2.

The study of Holliger and Devillers (1981) indicated that temperatures in the reaction zone were of the order of 280 +/-50°C.

The temperature estimates of Openshaw et al. (1978) based on a study of fluid inclusions were discredited by Gauthier-Lafaye and Weber (1984).

2.2.3 Relevant Uranium Deposits

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2.3 Geologic Nuclear Parameters

2.3.1 Natural Reactor Identification

Kuroda, P.K., 1975. Fossil nuclear reactor and plutonium - 244 in the early history of the solar system. The Oklo Phenomenon, International Atomic Energy Agency, Vienna, 1975, p. 479.

Balagna, J.P., G.A. Cowan, 1978. A non-destructive field measurement of the $^{235}U/^{238}U$ ratio in depleted to moderately enriched uranium, Les Reacteurs de Fission Naturels, International Atomic Energy Agency, Vienna, p. 391.

Maeck, W.J., J.E. Delmore, R.L. Eggleston, F.W. Sparktes, 1978. The measurement of Ruthenium in uranium ores and ^{238}U spontaneous fission yields, Les Reacteurs de Fission Naturels, International Atomic Energy Agency, Vienna, p. 521.

Maeck, W.J., K.E. Apt, G.A. Cowan, 1978. A possible Uranium-Ruthenium method for the measurement of ore age, Les Reacteurs de Fission Naturels, International Atomic Energy Agency, Vienna, p. 535.

Naudet, R., 1978. Etude parametrique de la criticite des reacteurs naturels, Les Reacteurs de Fission Naturels, International Atomic Energy Agency, Vienna, p. 589.

Apt, K.E., J.P. Balagna, E.A. Bryant, G.A. Cowan, W.R. Daniels, R.J. Vidale, D.G. Brookins, 1978. Search for other natural fission reactors, International Atomic Energy Agency, Vienna, p. 677.

McLaren, K.G., 1978. The Oklo Phenomenon-Natural Nuclear Reactors, Search, Vol. 9, No. 8-9, p. 301.

Bouzigues, H., Boyer, R.J.M., Seyve, C. and Teulieres, P., 1975. Contribution to the solution of a scientific enigma. The Oklo Phenomenon, International Atomic Energy Agency, Vienna, p. 237.

The possibility of an Oklo-type natural fission reactor existing two-billion years ago was predicted by P.K. Kuroda of the University of Arkansas in 1956. Nuclear chain reaction could have occurred in any high-grade (above 20%) uranium deposits older than one-billion years. The spatial distribution of the uranium concentration must be such as to create zones with surface area-to-volume ratios which ensure a sufficient neutron loss-to-neutron production ratio: zones of approximately 1 m^3 in size fulfill the condition. This is conditional to the absence of uranium minerals monazite and carnotite containing vanadium and thorium or of other neutron poisons such as cadmium, boron or lithium. On the other hand, the presence of carbon and/or water is required for neutron moderation. Were all these conditions met at the time when ^{235}U content of the uranium was around 3.25%, nuclear fission must have occurred in the ore body. Because of the high ^{235}U isotope content of uranium two-billion years ago, numerous uranium deposits must have existed in a state of potential criticality during earlier Precambrian time.

From the field techniques developed for detection of natural fission in uranium, the measurement of ruthenium isotopes proved to be the most sensitive. The method is based on the understanding that the ratio of isotopes of mass 99, 101, 102 and 104 is significantly different from the ratio of the Ru isotopes derived from ^{235}U neutron induced fission. The ruthenium resulting from ^{238}U spontaneous fission can be determined from this ratio. For fast, on-site monitoring, an instrument measuring the relative fission rates of ^{235}U and ^{238}U in fast and moderated neutron spectrum ranges was constructed.

Since the discovery of the Oklo reactor by Bouzigues and his team at the gas diffusion plant at Pierrelatte in 1972, a thorough search for other geologic nuclear reactors was carried out concentrating on Auscralian and Canadian deposits. However, no other reactors than those at the Oklo site were found.

2.3.2 Methods

Naudet, R., 1974, Les reacteurs naturels d'Oklo. Bilan an 1er Mai 1974, Bulletin d'Informations Scientifiques et Techniques du CEA, Paris, No 193.

In the initial work on the Oklo Phenomenon, summarized by Naudet in 1974, it was stated that if detailed isotope geochemical data become available for the Oklo ore body, the age, duration, extent of the nuclear reaction, and the spectrum of neutrons should be estimable. In

order to investigate these parameters, new approaches applicable to geologic systems had to be worked out, neutron physical calculations and analytical techniques had to be adapted. These topics comprised the isotope geochemistry and neutron physics sections of the Oklo Phenomenon Symposium in 1975.

Naudet, R., A. Filip, 1975. Interpretation neutronique des distributions de taux de reaction dans les reacteurs d'Oklo. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 557.

Naudet, R., 1975. Mechanismes de regulation des reactions nucleaires Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 589.

Naudet, R., A. Filip, 1975. Etude du bilan neutronique des reacteurs naturels d'Oklo. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 527.

Havette, A., R. Naudet, G. Slodzian, 1975. Etude par analyse ionique de la repartition et des proportions isotopiques de certains elements dans des echantillons d'Oklo. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 463.

Neuilly, M., R. Naudet, 1975. Etude de la distribution des fluences dans les reacteurs naturels d'Oklo, par analyse isotopique des terre rares. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 541.

Ruffenach, J.C., J. Menes, M. Lucas, R. Hagemann, G. Nief, 1975. Analyses isotopique fines des produits de fission et determination des principaux parametres des reactions nucleaires. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 371.

Bassiere H., J. Cesario, D. Poupard, R. Naudet, 1975. Analyse isotopique et ponderale de terres rares dans divers echantillons d'Oklo. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 385.

Hagemann, R., C. Devillers, M. Lucas, T. Lecomte, J.C. Ruffenach, 1975. Estimation de la duree de la reaction. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 423.

Ion probe studies by Havette et al (1975) proved useful for the first calculations of nuclear parameters when they demonstrated that the ion probe images of ^{235}U and ^{238}U in samples from reactor zone 2 coincided. This was an indication that all the fissile nuclides (including ^{239}Pu which decayed to ^{235}U) remained in their original location. They found the same for Pd, Y and Nb which was formed in the uranium ore.

A systematic analysis of the neodymium transformation $^{143}Nd \rightarrow {}^{144}Nd$ by spark-source mass spectrometry was carried out by Neuilly et al (1975) in order to establish the integrated neutron flux (fluence) during the time of reaction. Neodymium has the highest fission yield of the rare elements which makes it an ideal choice for thermal neutron fluence

calculation. When Neuilly correlated the isotopic depletion of uranium across the reactor zone No 2 (in core SC-36), he found the ^{235}U depletion to be less than expected for the estimated fluence and corresponding fission. Thus, in order to match the measured $^{235}U/^{238}U$ ratio in addition to the thermal, the resonance and fast neutron fluences had to be also considered. He concluded that ^{238}U was transformed by neutron capture and beta decay into fissile ^{239}Pu which decayed to ^{235}U. Evidently, there was sufficient time for ^{239}Pu (half-life 24 400 years) to decay to ^{235}U which indicated that the reaction rate was very slow. The conversion of ^{238}U to ^{235}U via ^{239}Pu occurred with a characteristic conversion factor of $C = 0.45$. This factor quantifies the ratio of neutron capture in ^{238}U to ^{235}U destroyed. Conversion coefficients found by Hagemann were between $C = 0.4-0.6$. It was possible to account for the amount of ^{235}U found when the ^{235}U cross section was decreased by the factor (1-C).

There was a correlation between the conversion factors and neutron spectrum indeces (defined as the ratio of the reaction rates of ^{143}Nd and ^{147}Sm). The relation between the isotopic depletion and uranium concentration was not so straightforward: in the centre of the reactor zone the minimum depletion coincided with a maximum of uranium concentration. Naudet et al (1975) were able to account for this mathematically as an effect resulting from the local under-moderation of the neutrons. On the whole, the neutron fluence across the reactor zone appeared to be more uniform than the distribution of $^{235}U/^{238}U$ depletion, since a significant variation of the conversion factor C was superimposed on the latter.

Ruffenach et al (1975) analyzed the isotopic composition of rare earths Nd, Sm, Gd by spark-source mass spectrometry in two samples (KN50-3548) from the core of the reactor zone 2 and in four samples from core SC-36 taken across the reactor zone. Four samples were also analyzed for Ru and one sample for Pd isotopes. Additional samples were studied by the same technique by Bassiere et al (1975). The isotope data on Nd and Sm were then used to calculate the integrated neutron flux. In reactor zone 2, the fluence exceeded $10^{21} n/cm^2$ with a low mean neutron flux in the order of $10^{7} n/cm^2$ sec.

As the dependence of neutron capture cross section on energy is known, the measured isotope abundances indicate the neutron spectrum which existed in the reactor zone. The measured isotopic abundances of Nd and Sm gave a well-thermalized neutron spectrum with a spectral index between 0.15 - 0.25.

Hagemann et al (1975) reported difficulties encountered when determining the fission contribution of $^{238}U(\alpha)$ and $^{239}Pu(\beta)$ from the isotope composition of Gd, Sm, Nd, Ru and Pd.

In 1975, Ruffenach estimated from $^{110}Pd/^{105}Pd$ and $^{110}Pd/^{106}Pd$ pairs were $\alpha = 7\%$ and $\beta = 5\%$. However, the best estimates from all the measured fission product pairs were $\alpha = 2.5\%$ and $\beta = 4\%$. Despite these difficulties, it was possible to dependably conclude that ^{235}U accounted for more than 90% of the fission.

The duration of the reaction was calculated by Ruffenach et al (1975) from the $^{150}Nd/^{143}Nd+^{144}Nd$ ratio and from a conversion factor C = 0.48 which was derived from ^{239}Pu fissioned. Based on the assumption of a constant flux over the critical period they arrived at the conclusion that the reaction lasted for at least 600 000 to 800 000 years in the reactor zone 2. Nevertheless, the dependability of the results is somewhat limited since the fraction of ^{239}Pu fission products and of the ^{238}U fast fission products is very small and, therefore, the relative error of estimation rather high.

For most of the rare earth elements the conditions of retention in the uraninite are met. Thus, the measurements of the absolute content of these isotopes can be used for estimations of the fluence. The most reliable calculations are obtained from the neodymium isotope spectrum. Making use of this fact, Devillers and Naudet (1975) calculated from the fluence the number of U atoms which underwent fission and related it to the number of ^{235}U atoms available in the uraninite at the end of the reaction. Despite uncertainties concerning the effective fission cross section of ^{235}U which is dependent on the energy spectrum, they arrived at an age of 2000 million years. This estimate comes close to the geochronological age of the reactor.

The long duration of the nuclear reactions in the Oklo deposit was controlled by the quantities of neutron poisons (Boron and the rare earths Samarium and Gadolinium) and the moderator (water) present. The amount of poison had to be low enough to enable a chain reaction, but sufficiently high to keep the average reaction rate low. The control by neutron poisons is, however, an unstable mechanism. A more stable control was provided by the water impregnating the formation, which served as a moderator and maintained the neutron balance. Whenever the energy production increased above an equilibrium value, sufficient water was driven out of the reaction zone to under-moderate the reaction and decrease the neutron multiplication coefficient. Decrease of energy output and dissipation of excessive heat facilitated the return of the water.

The propagation of reaction was made possible by neutrons diffusing to the minerals adjacent to the uraninite involved in the reaction and destroying the neutron poisons so that criticality could be achieved later. The average range of escaping neutrons was around 12 cm. After destruction of neutron poisons, the reactivity within the uranium rich zones diminished as a direct function of neutron irradiation.

By studying the variation of the neutron multiplication coefficients as a function of uranium concentration with the water quantity as a parameter, Naudet et al (1975) calculated the combination of values consistent with the requirements of a maintained criticality. Water contents of 10 - 25% were considered.

2.3.3 Data

Maeck, W.J., F.W. Spraktes, R.L. Tromp, J.H. Keller, 1975. Analytical results, recommended nuclear constants and suggested correlations for the evaluation of Oklo fission-product data. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 319.

Loubet, M., C.J. Allegre, 1977. Behaviour of rare earth elements in the Oklo natural reactor. Geochimica et Cosmochimica Acta, Vol. 41, p. 1539.

Frejacques, C., C. Blain, C. Devillers, R. Hagemann, J.C. Ruffenach, 1975. Conclusions tirrees de l'etude de la migration des produits de fission. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 509.

Cowan, G.A., E.A. Bryant, W.R. Daniels, W.J. Maeck, 1975. Some Unite States studies of the Oklo Phenomenon. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 341.

The main obstacle, as stated by Maeck (1975), concerning a precise interpretation of the geochemical data on elements and isotopes is twofold:

(1) the measurements obtained from at least ten various laboratories cannot be inter-correlated because of technical differences in their approaches,

(2) different authors used different values of nuclear constants for their calculations according to the local usage.

Generally, a synthesis of the results is not overly reliable as the data base is neither uniform nor consistent. Especially, precise data on fission and capture cross-sections of the relevant nuclides were lacking. In addition, the elements in Oklo samples can be assumed to be a mixture of (1) natural element composition of the pre-reaction stage, (2) reaction produced, and (3) post-reaction contamination. The fluence values are not affected by loss of elements after the reaction time as migration normally occurs without isotopic fractionation. However, corrections must be applied to the analytical results for

(1) the natural background before criticality, and

(2) the neutron capturing during reaction.

The nuclear parameter data tend to be more reliable when these contaminations are minimal.

According to Loubet et al (1977), post-reaction contamination of the rare earth elements did not occur for Nd and Sm. For Gd, Dy (possibly Er and Yb) and Lu a contamination (associated with migration) could have occurred up to 20-30%.

Cowan et al (1975) analyzed samples mainly from the 2'P' horizontal traverse and SC-36 vertical borehole (both zone 2) and derived (1) the age from the time the reaction started, t_o = (1.84± 0.07) b.y.; but the data remained consistent also within the range of 1.6 to 2.1 b.y.; (2) the duration of criticality, d = (0.23+/-0.07) m.y. with the lowest possible limit of 0.2 m.y.; with likely longer duration than the average value; (3) the thermal neutron fluence τ, resonance fluence ratio, R and conversion factor, C for the 2'P' traverse:

τ = (1.57 to 1.93) x 10^{21} n/cm^2

R = 0.0082 to 0.034

C = 0.35 to 0.66

for the SC-36 core:

τ = (0.53 to 0.77) x 10^{21} n/cm^2

R = 0.031 to 0.050

C = 0.19 to 0.75

The authors also considered a fractional accretion rate of uranium during the reaction and the fraction of uranium loss since criticality.

Part of the samples studied by Cowan et al (1975) was analyzed also by Maeck et al (1975). The measured data on isotopic abundance of ^{235}U, fission density of total residual U and neodymium isotope ratios 144/143 and 146/145 were tested in concordant diagrams as a function of fluence and effective resonance flux. The results are specially valuable because a consistent set of fission and capture cross-sections and resonance integrals was used when the fluence and resonance flux were calculated. The combinations of fluence and resonance flux which yield the measured data were within the range of 0.174 to 1.23 x 10^{21} n/cm^2 fluence and 1 to 4% resonance flux when ages of 1.8 x 10^9y and 1.9 x 10^9y were considered. Reasonable concordance for the data existed when durations of 1 x 10^5 to 3 x 10^5y were considered.

Ruffenach, J.C., J. Menes, C. Devillers, M. Lucas, R. Hagemann, 1976. Etude chimiques et isotopiques de l'uranium, du plomb et de plusieurs produits de fission dans un echantillon de minerai du reacteur naturel d'Oklo, Earth and Planetary Science Letters, 30, p. 94.

Gancarz, A.J. 1978. U-Pb Age (2.05 x 10^9) years of the Oklo uranium deposit. Le Reacteurs de Fission Naturels. International Atomic Energy Agency, p. 513.

Lancelot, J.R., Vitrac, A., Allegre, C.J., 1975. The Oklo natural reactor: age and evolution studies by U-Pb and Rb-Sr Systematics, Earth and Planetary Science Letters 25, p. 189.

Devillers, C., J.C. Ruffenach, J. Menes, M. Lucas, R. Hagemann, G. Nief,

1975. Age de la mineralisation de l'uranium et data de la reaction nucleaire. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 293.

Devillers, C., J. Menes, 1978. Contribution du plomb et du thorium a l'histoire des reacteurs d'Oklo, Le Reacteurs de Fission Naturels, International Atomic Energy Agency, p. 495.

An extensive re-evaluation of the 1975 preliminary data was undertaken by Ruffenach et al (1975). One sample from the core of the zone 2 (KN 50-3548) was investigated in great detail for isotopic composition of Nd, Gd and Sm; in addition, Eu, Kr and Xe were measured. The most important result was an improved concordance of the fission product pairs, giving new values for the fission contribution of $^{238}U(\alpha)$ and $^{239}Pu(\beta)$

$$\alpha = (2.5+/-0.5)\% \text{ and } \beta = (3.0+/-0.3)\%.$$

The values of Ru measurements were left out this time as the authors realized the possible disturbance due to migration of the ^{99}Ru parent nuclide ^{99}Tc.

Thus, the total number of fission which was estimated at (3.15+/-0.2)% per U atom could be broken down as

2.98% fission due to ^{235}U

0.08% fission due to ^{238}U

0.09% fission due to ^{239}Pu

From ^{235}U depletion the minimum neutron fluence of $\tau_{min} = 0.64 \times 10^{21}$ n/cm^2 was obtained. The neodymium isotope ratios as a function of fluence, τ and spectrum index, κ gave as best values

$$\tau = (1.25+/-0.01) \times 10^{21} \text{ n/cm}^2 \text{ and}$$

$$\kappa = 0.15+/-0.005.$$

The factor of conversion, C was calculated as C = 0.48+/-0.01. Using these values the age of reaction was calculated as t_o = 2000+/-100 m.y. This is the highest age calculated from nuclear parameters. It has to be pointed out, however, that the capture cross-section of ^{143}Nd used in calculations was very different from that used by Maeck (1975).

The same values used for calculation of the duration of criticality gave:

$$d = 0.6+/-0.1 \text{ m.y.}$$

The reactor's age of 2 billion years coincides with Gancarz's (1978) estimate of the U-Pb age of the Oklo deposit as $(2.05+/-0.03) \times 10^9$ years.

The measurements were done on 10 samples peripheral to the reactor zone. The evaluation allows for Pb loss with a diffusion constant $D/a^2 = 3.5 \times 10^{-11}$ which gives a more realistic estimate than the ill-defined ages by Lancelot et al (1975) and Devillers et al (1975) assuming a closed system. Devillers et al in their 1978 paper considered in the age determination the possibility of Pb migration and in view of the Th/U balance re-evaluated the age of the Oklo deposit as greater than 1.9×10^9 years. The Nd/U balance supported the conclusion of a greater age than 1.93×10^9 years. Should it turn out that the age of the reaction and the geochronological age of the formation is the same, it would support the hypothesis that criticality was achieved during or close to the end of the secondary mineralization.

Lucas, M., R. Hagemann, R. Naudet, C. Renson, C. Chevalier, 1978. Determinations des sections de capture neutronique d'isotopes intervenant dans le phenomene d'Oklo par irradiation dans le reacteur Triton, Le Reacteurs de Fission Naturels, International Atomic Energy Agency, p. 407.

Neuilly, M., J.F. Dozol, R. Naudet, 1978. Nouvelles mesures de distribution des fluences dans les reacteurs d'Oklo par analyse isotopique des terres rares, Le Reacteurs de Fission Naturels, International Atomic Energy Agency, p. 433.

Ruffenach, J.C., 1978. Les reacteurs naturels d'Oklo, Les reacteurs de fission naturels, International Atomic Energy Agency, Vienna, p. 441.

Cesario, J., D. Poupard, R. Naudet, 1978. Nouvelles analyses des terres rares dans des echantillons d'Oklo. Les reacteurs de fission naturels, International Atomic Energy Agency, Vienna, p. 473.

As was pointed out earlier, the uncertainties in calculation of nuclear parameters depend greatly on knowledge of capture cross-sections and on the quality of the rare earth measurements.

In order to obtain accurate values of the effective capture cross-section as a function of the neutron spectrum, Lucas et al (1978) undertook their measurement for all the relevant nuclides. The measurement of ^{143}Nd confirmed the value used previously for calculation of fluences by both the French and American authors. The capture cross-section of ^{147}Sm was smaller than previously quoted by American authors and used for determination of spectrum indeces. The resonance integral wf ^{99}Tc was significantly smaller than that quoted by American sources. This changes the calculation of duration of criticality.

The systematic rare earth isotopic analyses carried out by Neuilly et al (1978) were mainly aimed at making more precise the fluence measurements as a function of distribution of uranium isotopic depletion. The samples were taken from 5 cores (SC 39, 35, 43, 63, 30) intersecting the reactor zone. When calculating the fluence from the rare earth measurements, the new capture cross-section values measured by Lucas et al (1978) were used. The uranium content (concentration values from 9

to 60%) and ^{235}U depletion (from 0.402 to 0.686%) correlated with the fluence values from 0.36 to 1.44 x 10^{21} n/cm^2. Local shifts between the U depletion and fluence curves indicate small scale redistribution of the rare earths in the border areas but also within the reactor.

Further refinement of the nuclear data was carried out by Ruffenach (1978) when he analyzed samples from borehole SC-36 intersecting zone number 2 for U, Nd, Sm, Eu, Gd and Dy. A close study of U, Nd, Sm and Gd distribution across the reactor zone shows very similar patterns. However, small redistribution occurred on the borders and in the centre of the zone. A detailed study of the difference between measured and calculated fission product amounts compared to the average value in the centre of the zone gave the extent of remobilization. About 3-5% of the fission-produced Nd was mobilized. Up to 15% to 20% of Gd and of the heavier rare earths were redistributed. The redistribution always remained under 80 cm. This small scale of redistribution did not invalidate the nuclear parameters derived from rare earth measurements and the recalculation of data from previous measurements of Ruffenach et al (1976) gave essentially the same values. For the high ^{235}U depletion zone 2 fluences between 0.51 and 1.45 x 10^{21} n/cm^2 were calculated. The number of fissions per atom of total uranium is high, about 3%. All rare elements studied lead to about the same age of little less than 2 x 10^9 years for the zone 2. The duration of criticality was about 0.58 to 0.95 x 10^6 years, but was probably not continuous. This long duration of criticality indicates that in spite of high fluences, the prompt neutron flux at Oklo was only around 10^7 n/cm^2 s.

Nearly 40 samples analyzed for rare earth isotopic composition by Cesario et al (1978) support the findings of Ruffenach.

Naudet, R., C. Renson, 1978. Bilan descriptif des reacteurs d'Oklo. Les reacteurs de fission naturels, International Atomic Energy Agency, Vienna, p. 151.

Naudet, R., 1978. Etude neutroniques complementaires sur le phenomene d'Oklo. Les reacteurs de fission naturels, International Atomic Energy Agency, Vienna, p. 569.

Holliger, P., C. Devillers, G. Retali, 1978. Evaluation des temperatures neutroniques dans les zones de reaction d'Oklo par l'etude des rapport isotopiques $^{176}Lu/^{175}Lu$ et $^{156}Gd/^{155}Gd$, Les reacteurs de fission naturels, International Atomic Energy Agency, Vienna, p. 553.

Holliger, P., C. Devillers, 1981. Contribution a l'etude de la temperature dans les reacteurs fissiles d'Oklo par la mesure du rapport isotopique du lutetium. Earth and Planetary Science Letters, 52, pp. 76-84.

Naudet, R., 1978. Prise en compte des effets thermiques dans l'etude du controle et de la propagation des reactions nucleaires, Les reacteurs de fission naturels, International Atomic Energy Agency, Vienna, p. 601.

Generally lower reaction rates, and therefore shorter duration of criticality, existed in the reaction zones 3 and 5 (south of zone 2). Despite high local uranium concentration, the ^{235}U depletion was lower than in zone 2 and accordingly the fluences rarely exceeded 0.5 x 10^{21} n/cm^2.

Naudet et al (1978) explained these observations by differences in the geometry of the reaction zones. The reaction zones south of zone 2 have a much smaller thickness of clay and fewer interruptions and irregularities in the uranium concentration. The transition region in these reaction zones can be related to the spatial distribution of fluence and spectral indices.

The improved neutron balance modelling by Naudet (1978) resulted in a better adjustment of the modelled flux distribution to variations in the geological characteristics of the reaction zone. From the corresponding spectral indices and conversion coefficients, the distribution of neutron poisons at the time of the reaction and of water during criticality was approximated. The likely porosity of the reaction zones during criticality was 30%. Water contents below 12% were considered too low for efficient neutron moderation. On the other hand, water contents above 16% would have caused a too diffuse neutron flux to maintain criticality. In the model of the control mechanism of the nuclear reaction as described by Naudet (1975), the temperature of the reaction played the key role by affecting the moderating ratio through modification of the density of water.

The temperature conditions during criticality were evaluated by Holliger et al (1978, 1981) by a strictly nuclear approach. The ^{176}Lu capture cross-section is particularly sensitive to the average equilibrium temperature as a result of neutron generated heat in the moderator and therefore measurements of the $^{176}Lu/^{175}Lu$ ratio can be used as an indicator. The reliability of the estimation is subject to the non-migration condition of uranium and rare earths, and strongly dependent on the precise knowledge of the capture cross-section as a function of the neutron energy spectrum. For the reaction zone 2, 3 and 5 neutron temperatures of at least 280 to 400°C were estimated.

Since it appears that the reaction took place under a thick geologic cover, Naudet (1978) expects the water in supercritical state at temperatures around 350 to 400°C. He assumed an equilibrium between the heat generated by the reaction (at the temperature level required for criticality) and heat removal flux from reactor.

Convection currents were likely to have directed the propagation of the reaction in direction opposite to the one in which they were moving. Thus, the individual zones achieved criticality sequentially.

2.4 Migration/Retention

2.4.1 Elements and Isotopes

Walton, R.D., G.A. Cowan, 1975. Relevance of nuclide migration at Oklo to the problem of geologic storage of radioactive waste, Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 499.

Brookins, D.G., M.J. Lee, B. Mukhopadhyay, S.L. Bolivar, 1975. Search for fission-produced Rb, Sr, Cs and Ba at Oklo, Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 401.

Maeck, W.J., F.W. Spraktes, R.L. Tromp, J.H. Keller, 1975. Analytical results, recommended nuclear constants and suggested correlations for the evaluation of Oklo fission-product data. Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 319.

Walton et al (1975) concluded after making spark source mass spectrometric measurements on samples from the SC-36 and SC-23 cores that

Kr, Xe, I migrated most extensively

Mo migrated (however, the process was not fully understood)

Zr was mostly retained but experienced partial migration

Y and Nb were probably completely retained

Rare earths and Ce were retained.

The interpretation of Cs was ambiguous as there was less ^{133}Cs measured than predicted from fission yield calculations. However, this could be due to the difficulty of differentiating the fissiogenic ^{133}Cs from natural Cs which consists of 100% ^{133}Cs.

Brookins et al (1975) while investigating samples from the 2'P' cross-section by thermoionic mass spectrometry and trying to quantify the retention encountered the following problems: there were oxidation coatings along virtually all surfaces and in fine cracks which contaminated the samples. The large amounts of alkali and alkaline earths in the gangue minerals surrounding and infiltrating the ores further complicated evaluations. Nevertheless, the authors could show

1 to 10% retention for Rb

0.5 to 5% retention for Sr

some retention for Cs and Ba

in the uraninite grains. In fact, there was a ^{135}Ba and ^{137}Ba enrichment compared to the fissiogenic ^{135}Cs and ^{137}Cs. The insoluble residues showed a decreasing $^{85}Rb/^{87}Rb$ ratio with increasing $^{135}Ba/^{137}Ba$ indicating retention. The Ba which migrated ended very likely in barite

which was reported to be present in the ore body.

Among the first quantitative isotope-dilution mass spectrometric measurements of fission products are those of Maeck et al (1975). In addition to rare earth measurements (for reference purposes) they investigated the isotopic composition of Rb, Sr, Zr, Ho, Ru (Tc) on samples from the 2'P' traverse, SC-36 and SC-32 cores and 21 traverse. It is not possible to obtain reliable quantitative data in all the cases. One of the problems was that the isotopic composition was too highly perturbed from neutron capture on the natural component. Nevertheless, they stated the following migration behaviour:

Rb (product of Cs)	60% migration due to solubility
^{90}Zr (product of ^{90}Sr)	5% migration due to replacement
^{93}Mo	90% migration due to solubility
Ru	limited migration
^{99}Ru (product of ^{99}Tc)	5-20% migration due to solubility but otherwise retained in place or very locally redistributed. The mobile Zr tended to concentrate in the clay of the reaction zone.

Frejacques, C., 1975. Conclusions drawn from studies on the Oklo natural reactor concerning the evolution in the ground of radioactive waste over a long period, 1st Conference of the European Nuclear Society, Paris, p. 695.

Frejacques, C., C. Blain, C. Devillers, R. Hagemann, J.C. Ruffenach, 1975. Conclusions tirrees de l'etude de la migration des produits de fission, Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 509.

Frejacques, C., R. Hagemann, 1976. Conclusions from studies of the Oklo natural reactors, Proc. Int. Symp. on the Management of Wastes from LWR Fuel Cycle, Denver, p. 678.Dran, J.C., M. Maurette, J.C. Petit, R. Drozd, C. Hohenberg, J.P.

Maeck, W.J., 1978. Table roude, Les Reacteurs de Fission Naturels, International Atomic Energy Agency, Vienna, p. 675.

Hagemann, R., C. Devillers, T. Lecomte, 1978. Interpretation des analyses chimiques et isotopiques du Ruthenium effectnees sur des echantillons d'Oklo et sur des echantillons d'origines geologiques variees, Les Reacteurs de Fission Naturels, International Atomic Energy Agency, Vienna, p. 543.

Hagemann, R., R. Naudet, F. Weber, 1980. Enslignements tires de l'etude des reacteurs naturels fossiles d'Oklo pour le stockage des dechets radioactifs, underground disposal of radioactive wastes, Vol. 2, International Atomic Energy Agency, Vienna, p. 223.

Ruffenach, J.C., R. Hagemann, E. Roth; 1980. Isotopic abundances measurements a key to understanding the Oklo phenomenon, zeitschrift fur Naturfurschung, 35a, p. 171.

Already before the Libreville Symposium Frejacques (1975) made some preliminary conclusions concerning the migration of elements using results obtained at Saclay from the core SC-36. These conclusions were reconsidered and extended by Frejacques and Hagemann (1975, 1976), to be summarized as follows:

Up to 99.0% or 99.99% of the rare gases Kr, Xe disappeared. Their migration must have taken place during the reaction as they show lower fluences than estimated. The volatile I showed a similarly extensive migration as evident from the remnant daughter products ($^{129}I \rightarrow ^{129}Xe$, $^{131}I \rightarrow ^{131}Xe$).

The alkali metal and alkaline earth oxides Rb, Cs, Sr, Ba which are insoluble in the UO_2 matrix were extensively replaced by natural elements and this first hindered conclusions concerning migration of ^{135}Cs and ^{137}Cs. The $^{135}Ba/^{137}Ba$ ratio was used by Frejacques and Hagemann (1975, 1976) to point out the excess of this ratio above the same ratio in natural barium. As the half-lives of ^{135}Cs and ^{137}Cs are 2.6×10^6 and 30 years, the observed excess of the decay-produced Ba suggests at least partial Cs retention for about 10 half-lives of ^{135}Cs, that is 26×10^6 years.

From a slight deficiency of about 5% of ^{90}Zr, a limited migration of the parent ^{90}Sr prior to decay (by a half-life of 28 years) was deduced.

Precious metals Ru, Rh, Pd, Ag were well retained, probably as metallic inclusions, except for ^{99}Ru from the decay of ^{99}Tc (half-life 2.13×10^5 years) which showed a 20 to 30% deficiency compared to other Ru isotopes. A marked differentiation between Ru and Tc along the borehole Sc-36 of zone 2 was observed by Hagemann et al (1978) thus clarifying that the migration affected Tc but not Ru.

It is for this reason that about 10 to 15% of Ru is missing from the reaction zone and some of it can be found in association with the argillites and spread as far as 2 to 5 metres from the reaction zone (Maeck, 1978).

Molybdenum obviously formed an oxide which was not soluble in the UO_2 matrix and therefore suffered extensive migration (Maeck, 1975). Oxides soluble in the UO_2 matrix were formed by fission products Y, Nb, Zr and the rare earths and remained immobile with the partial exception of Zr which suffered some remobilization in the order of 30% (Frejacques, 1975).

Brookins, D.G., 1981. Alkali and alkaline earth element studies at Oklo, Scientific Basis for Nuclear Waste Management, Plenum, New York,

p. 275.

Brookins, D.G., 1983. Migration and retention of elements at the Oklo natural reactor, Environmental Geology, 4, p. 201.

Alkali and alkaline earths were studied by Brookins (1981). A total of 32 samples from zones 2, 3, 4, 6/5 as well as from edges and areas between reaction zones were analyzed for Rb, Sr, Cs and Ba isotopes. The portion structurally bound in the UO_2 matrix was separated from the adsorbed portion of the fissiogenic elements before measurement. The migration of Rb from the reaction zone was not so far reaching as up to 60% of the fissiogenic Rb remained within a few metres of the point of origin. Only a small portion of fissiogenic Sr (less than 5%) remained bound to uraninite, the largest part was found loosely fixed at the edges of the reaction zone.

Extensive, although not total, retention of Cs was claimed for the duration of criticality and over 20-30 million years thereafter. A quantification is difficult because the fissiogenic Cs isotope is the same as the naturally occurring one.

The high natural Ba background makes fissiogenic Ba detection extremely difficult. Only questionable amounts of ^{138}Ba were measured and some ^{135}Ba (from ^{135}Cs) and ^{137}Ba (from ^{137}Cs) detected.

De Laeter, J.R., K.J.R. Rosman, 1975. Cumulative fission yields of cadmium in Oklo samples, Le Phenomene d'Oklo, International Atomic Energy Agency, p. 425.

De Laeter, J.R., K.J.R. Rosman, C.L. Smith, 1980. The Oklo natural reactor: cumulative fission yields and retentivity of the symmetric mass region fission products, Earth and Planetary Science Letters, 50, p. 238.

Loss R.D., K.J.R. Rosman and J.R. De Laeter, 1984. Transport of symmetric mass region fission products at the Oklo natural reactors, Earth and Planetary Science Letters, 68, p. 240.

Cd isotopes were measured by De Laeter et al (1975) in three samples from the reaction zones. The isotope analysis was carried out by using solid-source mass spectrometry; the elemental abundance was determined by stable isotope dilution technique. These measurements are of high accuracy due to the precision of the technique and careful evaluation of different types of fission contribution to the Cd balance. A significant loss of fissiogenic Cd in the order of 90% was stated right after the first measurements. However, some depletion of Cd could have been due to the large capture cross-section of ^{113}Cd resulting in increased ^{114}Cd.

Elements from the symmetric mass region of the fission yield curve (atomic mass 105 to 130), namely Pd, Ag, Cd, Su and Te were analyzed in

the extended investigations of De Laeter et al (1980). In samples from zones 2, 1 and 3 only extremely small amounts of natural Pd (^{102}Pd) and Sn were found. Natural Te (as indicated by ^{124}Te) was totally absent. Significant contaminations by natural Cd and Ag were recorded.

About 99.8% of fissiogenic Cd left the reaction zone. Only 20% of Ag and less than 40% of Sn remained in the reactor. The deficiency of ^{126}Te was interpreted as due to migration of the precursor ^{126}Sn. Te, in spite of its volatile nature, remained immobile. These measurements were extended by Loss et al (1984) by including additional samples from zones 2, 3/4, 5/6 and 7, as well as host rock samples. No quantitative estimates of Cd were possible in the host rock. A very small portion (0.1-0.6%) of fissiogenic Cd was found 20 m from the reaction zone, but generally no quantitative estimates of Cd were possible in the host rock. The isotopic composition of Te and Pd in the host rock showed only natural origin, thus supporting the conclusion that these elements were retained in the reaction zone. Because little evidence of fissiogenic Ag was found, the authors suggested that host rock samples closer to the reaction zones be analyzed.

Fissile Nuclides and their Decay Products

Frejacques et al (1975) suggests that Bi (formed from Np-decay) may have migrated in appreciable quantities, basing their argument on the fact that radiogenic Pd has been quite mobile. Lead redistribution was demonstrated to be local by Lancelot et al (1975).

Despite the proven stability of the host uraninite grains, a local redistribution of small amounts of uraninite may have taken place: Naudet (1978) pointed out the anomalous uranium isotopic composition around the reactor zones extending up to 2 m from the edge of the zone.

2.4.2 Conditions and Processes

Release

Eichenberg, J.D., P.W. Frank, T.J. Kisiel, B. Lustman, K.H. Vogel, 1958. Fuel Elements Conference, Paris, TID-7546, p. 616.

Thomas, G.F., G. Till, 1984. The dissolution of unirradiated UO_2 fuel pellets under simulated disposal conditions, Nuclear and Chemical Waste Management, Vol. 5, p. 141.

Duffy, C.J., 1978. Uranium solubilities in the Oklo reactor zones, Les Reacteurs de Fission Naturels, International Atomic Energy Agency, Vienna, p. 229.

Branche, G., F. Chautret, A. Guillemant, R. Pouget, 1975. Donnees chimiques et mineralogiques sur le gisement d'Oklo, Le Phenomene d'Oklo, International Atomic Energy Agency, Vienna, p. 119.

Durand, C. Le Gressus, D. Massignon, 1975. A multidisciplinary analysis of the Oklo uranium ores, Le Phenomene d'Oklo, International Atomic

Energy Agency, Vienna, p. 223, Krypton, Xenon.

Cowan, G.A., 1978. Migration paths for Oklo reactor products and applications to the problem of geological storage of nuclear wastes, Les Reacteurs de Fission Naturels, International Atomic Energy Agency, Vienna, p. 693.

Due to recoil, the release of about 10% of the light mass elements and about 5% of the heavy mass elements was calculated by Cowan (1978) for uraninite grains of 50 micron radius. An ion microprobe study of the uraninite grains by Duffy (1978) did not show any zonation with respect to the isotopic composition of the uranium. The ^{235}U depletion was homogeneous across the grains within a resolution width of 10 micron which indicated a negligible transport of uranium of natural composition toward the uraninite. This excluded dissolution and recrystallization of uranium as a major process of elemental release from the uraninite. Solubility calculations supported the conclusion, they were, however, carried out for 25°C only.

Using the fractions of elements retained in the UO_2 grains, Cowan (1978) accounted for the observed losses by assuming continuous diffusion with the following diffusion coefficients, D/a^2:

Elements	Retention	Diffusion, D/a^2
Pd, light T.R., Th Pu, Am, Cm	100%	5×10^{-12}/year
Nb, Zr, Ru, Ag, Te	10%	1×10^{-10}/year
Sr, Ba, Mo	0.1% to 10%	1 to 3.5 $\times 10^{-10}$/year
Kr, Rb, Xe Cs, Cd, I	0.01% to 1%	2.3 to 5 $\times 10^{-10}$/year
the major losses, however, could have appeared during the thermal period and continued at a slower rate afterward		
^{99}Tc	70% to 80%	10^{-7}/year
loss assumed only during criticality because of the half life 2.13×10^5 years		
Pb		3.5×10^{-11}/year

Based on the observation of Branche (1975) that only 5% of Pb which left the uraninite was retained (as galena) in the gangue (in spite of sufficient S present), Cowan (1978) assumed an equilibrium between Pb which left the uraninite and Pb which left the reaction zone. Under steady-state transfer the observed Pb (uraninite) to Pb (gauge) ratio of 10 can be explained by a flux out of the reaction zone with a diffusion constant of 3.5×10^{-9}/a.

Transport

Brookins, D.G., 1976. Shale as a repository for radioactive waste: the evidence from Oklo, Environmental Geology, Vol. 1, p. 255.

Brookins, D.G., 1978. Retention of transuranic and actinide elements and Bismuth at the Oklo natural reactor, Gabon: Application of Eh-pH diagrams, Chemical Geology, 23, p. 309.

Brookins, D.G., 1978. Eh-pH diagrams for elements from Z = 40 to Z = 52: Application to the Oklo natural reactor, Gabon, Chemical Geology, 23, p. 325.

Brookins, D.G., 1978. Application of Eh-pH diagrams to problems of retention an/or migration of fissiogenic elements at Oklo, Les Reacteurs de Fission Naturels, International Atomic Energy Agency, Vienna, p. 243.

Brookins, D.G., 1979. Thermodynamic considerations underlying the migration of radionuclides in geomedia: Oklo and other examples, Scientific Basis for Nuclear Waste Management, Plenum Press, New York, p. 355.

Brookins (1978a), assuming low temperature and low-pressure conditions at Oklo, constructed Eh-pH diagrams for Po, U, Pu, Am, (Eu), Np and Bi with thermodynamic data applicable for 25°C and 1 atm. First, however, he investigated the thermodynamic stability of some Fe- and S- species for low ionic strength solutions (Fe 10^{-6} m and S 10^{-3} m). The constraints for the Eh-pH field considered were derived from the coexistence of hematite, pyrite and carbonates in the Oklo ore body; the Oklo Eh-pH field extended along the pyrite-hematite in the pH range 7-8.5. As a result of the Eh-pH considerations, he asserted that Pu, Am, Np, Po, Bi could not have migrated at Oklo. He also disputed the results of Frejacques et al (1975) concerning Bi migration.

Using the assumption of 25°C and 1 atm, Brookins (1978b) constructed Eh-pH stability diagrams for Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te. Additionally, by assuming that solid solution of these metals in the UO_2 grains did not greatly affect the migrational behaviour, he concluded that there exists a good agreement between thermodynamic stability/instability of the species considered and migration/retention of elements observed. He claimed retention for Zr, Nb, Tc, Ru, Rh, Pd, Ag, In, Sn, Sb, Te; migration for Mo and Cd. He contradicted the conclusion of Frejacques et al (1975) about migration of ^{99}Tc.

Along the same line, Brookins (1978c) assumed overall low-temperature and low-pressure conditions for construction of Eh-pH stability diagrams for Y, rare earth elements (REE), Zr, Nb, Mo, Cd, Tc, Ru, Rh, Hg, Pd, In, Sb, Sn, Te, Bi, Pb, Np, Pu, Am. The Eh from -0.05 to 0.45 V and pH from about 7 to 8.5 he derived as relevant for conditions of migration. Brookins used the ionic activities of 10^{-3} mS, 10^{-2} mC, 10^{-6} m Fe, $10^{-3.5}$ m Si and 10^{-6} or 10^{-8} m for the elements considered. Under these conditions, he stated retention or very local redistribution for elements with ionic radii, charges and electronegativities, close to U (IV): Y, T.R., Zr, Nb, Rh, Sn, Pu, Np, Am as well as for chalcophile elements Ag, Tc, Ru, In, Sb, Te, Bi, Pd with the exception of Mo, Cd. He compared the migrational behaviour based on thermodynamic calculations to spark-source mass-spectrographic measurements by other authors and concluded that there was very good agreement between them.

Brookins (1979) repeatedly presented the Eh-pH stability of different chemical species for Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, REE, Pb, Bi, Po, Th, U, Np, Pu and Am at 25°C and 200°C, respectively (both at 1 atm). The conclusions from calculations at 25°C differ from his previous ones (Brookins 1978) for Mo, Cd, Pb, Bi by an increased mobility. The conclusions derived for 200°C conditions were markedly different from his previous conclusions (Brookins, 1978) for Zr, Mo, Tc, Ru, Cd, Sb, Pb and Bi, indicating a higher mobility. The Eh-pH diagrams were not presented.

Brookins, D.G., 1980. Geochemical aspects of radioactive waste disposal, Springer-Verlag, Heidelberg.

In his compendium on geochemical aspects of nuclear waste management, Brookins (1980) presented the calculations and Eh-pH diagrams of U stability at Oklo for 25°C, 100°C and 200°C at 1 atm. Also, the Eh-pH diagrams for Am, Np and Pu at 25°C and 1 atm were constructed. The calculation of stability of these elements at higher temperatures was not attempted because of the unreliability of data for species known at 25°C, disproportionation effects, possible radiolytic effects and uncertainties concerning relevance of species. Nevertheless, the Eh-pH conclusions at 25°C and 200°C for Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, REE, Pb, Bi, Po, Th, U, Np, Pu, Am from a previous paper (Brookins, 1979) were restated and compared with measurements presented by Naudet (1974), during the first Oklo meeting (1975) and by Gancarz (1980). The author claims good agreement between his conclusions and the observations for most elements.

The discussion of behaviour of specific elements at Oklo was repeated by Brookins in a later paper (Brookins, 1983); possible forms in which elements were retained can be summarized as follows:

stable sulfides:	Mo, Tc, Ru, Ag, Cd, In, Sb, Pd
oxides:	Nb, Tc, Ru, In, Sn
silicate (or oxide):	Zr
metal:	Rh, Te

Generally, the elements which were stable as insoluble oxides, silicates, or metals were the least mobile and the elements which precipitated as sulfides were only partially retained. The rest of the elements migrated away as ions or complexes. He suggested the study of three additional elements which were not considered before: Se, Br and Sb.

Gancarz, A., G. Cowan, D. Curtis, W. Maeck, 1980. ^{99}Tc, Pb and Ru migration around the Oklo natural fission reactors, Scientific Basis for Nuclear Waste Management, Plenum, New York, p. 601.

Gancarz et al (1980) measured 10 samples peripheral to the reactor zone (KN series and SCO) for Ru in order to evaluate ^{99}Tc migration. The relative abundances of ^{99}Ru (from ^{99}Tc), ^{101}Ru, ^{102}Ru showed that the samples to the east (stratigraphically below the reactor zones) were deficient in Ru and ^{99}Ru relative to uranium and at times deficient in ^{99}Ru relative to rutenium, thus indicating chemical fractionation due to ^{99}Tc migration. Samples to the west (stratigraphically above the reactor zones) were enriched in both ruthenium and ^{99}Ru. The traces of migration which can be followed to a 10 m distance from the reactor evidence that the transporting fluids must have moved from below the reactors across the zones in west-east direction. It can be deduced from the half life of ^{99}Tc that the migration which created the isotopic shift due to chemical Tc Ru fractionation lasted for 0.3 to 1.2 million years.

The mechanism of Pb migration was investigated. Authigenic pyrite was first analyzed in order to find out the initial (non-radiogenic) lead content at the time of formation of Oklo. Presently, the rocks at Oklo contain a mixture of initial and radiogenic lead which is rich in ^{207}Pb (from ^{235}U) and ^{206}Pb (from ^{238}U). The lead-uranium evolution diagram showed that relative to the concordia curve the basal conglomerates were enriched with lead and the lead-uranium fractionation in the ore was ongoing by continuous diffusion since the time of the reaction. The relation of radiogenic to common lead isotopes showed that both initial and radiogenic Pb isotopes migrated by diffusion over a distance of 3 to 5 m from the ore into the basal conglomerate.

Curtis, D.G., T.M. Benjamin, A.J. Gancarz, 1981. The Oklo reactors: Natural analogs to nuclear waste repositories, The Technology of High Level Nuclear Wastes, DOE/TIC-4621, p. 255.

Curtis et al (1981) considered several periods of migration:

(1) Thermal period lasting about 10^6 years during criticality and immediately after.

(2) Period of diagenesis lasting about 200×10^6 years defined as the time between age of uranium mineralization (2.05×10^9 years) - and the age of the pelite in the Francevillian series

(1.8×10^9 years).

(3) Period of ambient geologic conditions in the consolidated rock formation lasting 1.8×10^9 years.

Mass spectrometric measurements of the authors demonstrated that: A pervasive loss of elements took place from zone 2 resulting in an average escape of 26% of the fissiogenic ^{101}, ^{102}, ^{104}Ru and 34% of the mass 99 isotopes (corresponding to 100 kg Ru and 70 kg of mass 99).

In zone 3-4, the production and also the loss of these elements was an order of magnitude less than in zone 2 and only 8% of the fissiogenic Ru and 15% of the mass 99 isotopes were missing (corresponding to 6 kg Ru and 4 kg mass 99).

The loss of 2% to 30% of the fissiogenic Nd from zone 2 (no significant loss from zone 3-4) was also noted.

As the time limits for the escape of Ru and Tc were identified as subsequent to the period of nuclear criticality and prior to the end of the thermal period, it was possible to derive the diffusion coefficients. The effective coefficient for ruthenium (^{101}Ru + ^{102}Ru) was:

$$\text{zone 2:} \quad D/a^2 = 7.8 \times 10^{-8} \quad a^{-1}$$
$$\text{zone 3-4:} \quad D/a^2 = 2.5 \times 10^{-8} \quad a^{-1}$$

Diffusion coefficients for ^{99}Tc could not be calculated because the ratio ^{99}Ru/^{99}Tc was not known. However, when some reasonable assumptions were made, an effective diffusion coefficient comparable to that for ruthenium was calculated.

Differences in the element retention properties and the resulting differences in calculated diffusion coefficients, correlated with differences in the neutron fluences. The diffusion coefficients for ruthenium and technetium are two to three orders of magnitude greater than those calculated for lead. These differences probably reflected the temperature differences between ambient geologic conditions and the thermal conditions in the reactor zone.

An attempt was made to evaluate the transport and redeposition of the elements after release. The hydrogeochemical conditions were assumed to be in agreement with the stability field of the Oklo uranium ore by Brookins (1978). Then the temperature dependence of the equilibrium concentration of Nd^{+3}, TcO_4^-, RuO_4^{2-}, $Ru(OH)_2^{+2}$, UO_2^{2+} and PuO_2^{2+} in the Oklo fluid was evaluated. It was found that the oxidation of technetium to pertechnetate anions at 100°C to 150°C and of RuO_2 to RuO_4^{-2} at 250 to 425°C could account for the deficiency of these elements by transport during the thermal period. On the other hand, the retrograde temperature dependence of $Nd(OH)_3$ solubility suggests that neodymium was redistributed after the thermal period.

Because the absolute amounts of elements lost were approximately equal, it was considered more likely that the diffusional release rather than

the rate of subsequent migration was the controlling process.

The representative distances over which migration was observed are between 10 to 15 m.

The direction of movement of technetium relative to ruthenium was updip, which is consistent with mobilization by the convecting hot fluid. The direction of ruthenium migration is not so apparent. Thus, the order of migration rate follows as 10^{-5} m/a (10 m per 10^6 years). Assuming continuous flow of 10^{12} l of Oklo fluid through a 200 m^2 of rock which sustained an increased temperature for 10^6 years a fluid flow of 5 m/a followed. This approximate calculation leads to a sorption ratio of the order of 10^4 cm^3/g which is much larger than one would expect from laboratory experiments.

In the case of the Ru and Tc migration at Oklo, the retention was likely due to temperature dependent oxidation-reduction reactions during migration from the hot reactor zones to the geologic environment which was 150 to 200°C cooler and where the deposition of these elements took place when supersaturation at lower temperatures occurred.

Curtis, D.B., A.J. Gancarz, T.M. Benjamin, J.E. Delmore, 1982. LA-UR-82-1276.

After the new reactor zone number 9 was discovered in 1979, Curtis et al (1982) analyzed eight samples from the east and south side of the zone for Mo and Ru. Their mass spectrometric measurements indicated:

25% migration of $^{101} + ^{102}Ru$
35% migration of $^{99}Ru(^{99}Tc)$
80% migration of Mo

into the unirradiated ore body. Most of the fission products were retained within a distance of 1.5 m. The observed fractionation suggested the following mobility:

Tc > Ru > Mo

Curtis, D.B., 1984. Geochemical controls on ^{99}Tc transport and retention, workshop on radioactive migration. Natural Analogues to the Conditions Around a Final Repository for HLW. Chicago.

The ratios of $^{99}Ru/^{101}Ru + ^{102}Ru$ from the reactor zones 2, 3-4 and 9 and from the peripheral rocks demonstrated that technetium and ruthenium were fractionated from each other during the period of criticality. Reactor zone samples and samples from the aureoles within a metre of these zones were deficient in technetium; at distances between 1 to 6 metres, however, excesses of technetium existed. Under the stability conditions of uranium ore, technetium should have remained immobile as TcO_2. Three possible explanations could have existed for the observed

migration:

(1) Minerals capable of technetium retention may have been unstable under conditions in the reactor and stable under conditions of the geological environment. Differences in the chemistry and mineralogy of the reactor zone, the aureoles around them, and the unaltered host rock were documented.

(2) Reactor temperatures between 100°C and 200°C may account for the technetium deficiencies by the increase in solubility of the TcO_4^- species. This, however, does not explain the fractionation.

(3) Shifts in the redox potential induced by radiolysis may have oxidized technetium to soluble TcO_4^-. The same mechanism could explain the partial mobilization of uranium in the reactor zone. Oxidizing conditions were achieved due to removal of radiolysis produced hydrogen by iron which now exists preferentially in a reduced state in the reactor zones.

Technetium was subsequently retained under ambient geologic conditions in the peripheral rock.

Curtis, D.B., A.J. Gancarz, 1984. Radiolysis in the Oklo natural fission reactors, LA-Report.

The point is made that over 90% of ^{239}Pu did not fission at Oklo but underwent alpha decay producing radiolytic effects in the fluid. The uranium contribution to the alpha dose was small. There were, however, additional 10^{28} beta-gamma disintegrations from the fission products and ^{239}U decay, which contributed substantially to the dose during criticality.

In order to obtain the integrated eV doses per ton of fuel, the residual range and energy of the particles was approximated for the Oklo conditions and uraninite grain sizes of 250 and 500 m. The resulting total decay energy produced by all the relevant nuclides was

2.9×10^{25} MeV by beta
3.1×10^{25} MeV by alpha particles.

As the residual range for the betas was around 100 to 500 m (as opposed to 8.9 m for alphas) and as half of the beta energy can be assumed to have been absorbed in the water surrounding the uraninite grains, it appeared that the beta dose to water was 5 to 25 times that of the alpha dose.

Within the reaction zone 2, a rough correlation between radiation dose and extent of iron reduction was found. The plausible explanation for the ferrous iron was the reduction of ferric iron due to

the hydrogen produced by radiolysis which diffused into the clay of the reactor zone. The excess of ferrous iron in the reactor zone as compared to the Fe^{2+}/Fe^{3+} ratio in the regular Oklo rock may be related to the radiation yield of hydrogen gas. A maximum and minimum value can be calculated according to whether a transport of ferric iron into the zone and subsequent reduction or an in-situ solid state reduction is assumed.

The excess of radiolytic peroxide created by removal of hydrogen was used up by uranium, which was partially oxidized into its hexavalent form. It was shown that the 10% of uranium corresponding to 2.5×10^{26} atoms of uranium per ton of fuel in the reactor zone which migrated out of the reactor zone could satisfactorily complement the 5.4×10^{26} atoms of iron reduced per ton of uranium. Within the aureole the uranium was reduced and deposited. An increase of the Fe^{+3}/Fe^{+2} ratio in the same aureole accounts for the oxygen released due to uranium reduction.

The migration of some of the multivalent fission products (Mo, Tc and Ru) was then the result of their oxidation on the surfaces of uraninite grains which were surrounded by oxidizing remanants of radiolysis. These otherwise nonsoluble elements formed mobile oxyanions which migrated out of the reactor zone where they were reduced again.

3. SUMMARY

The Oklo natural reactors occur in more than two-billion year-old Proterozoic sediments which, although deformed in a brittle manner, are virtually unmetamorphosed. The history of development of the uranium concentration in the reactor zones involves potentially five events:

(1) primary deposition of uranium either as detrital grains of thorian uraninite or as concentration of biogenically enriched material, in a manner analogous to the deposition of uranium in the early Proterozoic Huronian of Canada and the Witwatersrand of South Africa.

(2) migration of hydrocarbons into fault bounded structural traps during the early structural development of the Francevillien (Connan, 1975; Gauthier-Lafaye and Weber, 1981).

(3) introduction of CO_2-rich fluids bearing uranium as uranylcarbonate complexes at temperatures less than 120°C, and the deposition of UO_2 as a result of the reduction and decrease in CO_2 content of the fluid by reaction with hydrocarbon material.

(4) deformation of the uranium-bearing strata and consequent development of a secondary permeability and porosity allowing concentration of uranium in structurally preferred sites.

(5) desilication of the secondarily enriched horizons leading to further enrichment of uranium in the reactor zones.

Conclusions concerning the geochemical processes at the natural reactors discovered in 1972 at Oklo required the determination of the following nuclear parameters:

(1) The initial pre-reaction abundances of uranium isotopes in the deposit which, because of radioactive decay, depend on the age of the reactor.

(2) The ratio of production and destruction of isotopes due to concurrent and competing processes of neutron capture and, when applicable, fission and radioactive decay, was determined by duration of criticality. A particularly sensitive indicator of the total (resonance plus thermal) neutron fluence was the $^{144}Nd/^{143}Nd$ ratio because of the approximately 100 fold larger neutron capture cross-section of ^{144}Nd, over ^{143}Nd.

(3) The change of the $^{235}U/^{238}U$ ratio due to its sensitivity to the neutron energy distribution had to be accounted for, in addition to the previous parameters. In particular, the capture cross-section of ^{238}U, which is 100 times greater for resonance than for thermal neutrons, proved to be of importance. This capture yielded considerable amounts of ^{239}Pu which partially fissioned (1% to 10%) but decayed predominantly to ^{235}U, resulting in a measurable increase in the $^{235}U/^{238}U$ ratio.

(4) The abundance of elements with large neutron capture cross-sections such as B, Cd, Gd, Sm (poisons), the relative quantity of neutron scattering elements such as hydrogen (moderator) and the absolute amount of uranium (fuel) determined the neutron energy distribution.

Consequently, the change of the geochemical inventory was estimated by measuring absolute or relative abundances of the relevant nuclides and by solving the Bateman equations describing their time-dependent losses and gains. The nuclear parameters were then iteratively adjusted to match the isotopic ratios or abundances of the parameter-sensitive nuclides such as ^{143}Nd and ^{238}U. It was possible to derive without great difficulty parameters such as fluences, spectrum indeces, proportions of nuclides that fissioned, as well as the duration of the reaction. A more problematic issue was the calculation of the age of the reaction from isotopic ratios of rare earth elements because knowledge of the absolute content of elements at the time of the reaction was required. From the present concentrations, the original concentration could only be derived with any reasonable certainty when it was assumed that the uraninite presented a chemically-closed system for uranium and for neodymium. As a working hypothesis, this was a reasonable assumption as the structure of uraninite remained essentially stable during and after criticality and even had the capacity to retain incompatible fission products in the mineral grains (Geoffroy, 1975).

The main emphasis before 1974 was on the development of methodology for the determination of nuclear parameters; therefore the data presented at

the Libreville Symposium must be considered as preliminary. Many of the measurements were actually semi-quantitative in nature. The data from spark-source mass spectrometric analyses lacked the precision for a detailed evaluation of nuclear parameters of the Oklo reactors. The work presented at the Technical Committee Meeting in Paris (1977) concentrated on the extension of the preliminary data base. Already at the Libreville Symposium in 1975 the fluences and conversion factors were satisfactorily estimated. Uncertainties remained concerning number of fissions, temperature and ^{238}U and ^{239}Pu participation in the fission and duration of criticality. The approaches and analytical techniques did not change. Compared to the normal $^{235}U/^{238}U$ ratio of 0.0072, the greatest and most extensive ^{235}U deficiencies were found in reaction zone 2. For this reason, the largest number of samples collected was from zone 2 and most of the nuclear data relate to this reaction zone. The average ^{235}U depletion was 0.005 to 0.006 with a maximum around 0.003, thus indicating that the largest number of fissions per gram rock and the highest neutron fluences occurred here. However, because natural components were present in the measured abundance of neodymium, only maximum and minimum values of neutron fluence could be determined. The thermal plus resonance neutron fluences were estimated to be as high as 10^{21} n/cm^2 and where overwhelmingly due to ^{235}U fission and, to a lesser degree, due to ^{239}Pu fission. The resonance proportion of the neutron fluence was small and the ^{238}U fast fission was of minor importance. From the homogeneity of uranium isotopic composition in rock samples, Naudet (1978) concluded that the mean distance for slowing neutrons from fission to thermal energy was in the order of centimetres.

The estimations of the age of the nuclear reaction were consistent within ranges from 1600 to 2000 million years (Cowan, 1975) and 1930 to 2500 million years. The general assumption was that criticality occurred soon after the uranium mineralization. The operating parameters of the reactor indicated that criticality lasted for 0.1 to 0.5 million years.

Conceptually, except for the elements used for evaluation of nuclear parameters, the Oklo reactor was considered an open chemical system. The retention of fission products in the reactor was then quantified relative to the amount of fissile nuclides and light rare earth elements which were considered immobile. Generally, the procedure used was as follows:

(1) The natural abundances were subtracted from the amount of isotope measured; the fission produced nuclides were obtained.

(2) The fission produced isotopes were related to the fission yield of the isotopes as calculated from the fissile nuclides (^{235}U, ^{239}Pu, ^{238}U); the relative abundances of the isotopes were derived.

(3) The relative abundances were related to the measured number of fissions based on ^{148}Nd measurement, which was assumed to be immobile.

(4) The extent of migration was quantified by the deviation of the relative abundance - to - ^{148}Nd ratio from unity. Ratios smaller than 1.0 were considered to indicate migration; ratios exceeding 1.0 indicated enrichment.

It was assumed that no isotope fractionation took place and therefore the isotope mobility could be taken as representing the mobility of the element. By using this approach, the migration/retention history of about thirty elements was reconstructed. The most extreme losses were found for rare gases, halogens, molybdenum and the alkali and alkaline earth elements.

There were three processes which could have led to the release of elements from the uraninite grains:

(1) knock-out due to fission recoil
(2) dissolution in water
(3) diffusion in the solid phase.

The recoil affected the fission fragments in an indirect proportion to their mass. This process could be expected to have released more light mass fissiogenic products (Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag) than heavy mass fissiogenic products (Te, Cs, Ba, REE, Ce) (Eichenberg et al, 1958). As nuclear fuel rod leachability considerations (Thomas and Till, 1984) suggest only minor uranium release, a release due to volume diffusion must be considered. Both processes were affected by the temperatures which existed at Oklo. Temperatures during criticality were, as indicated by fluid inclusion and rare earth studies (Openshaw et al, 1978, Holliger et al, 1978), somewhat above 400°C in the reaction zone and near 250°C in the adjacent ore body. The geothermal gradient at that time was around 40 to 50°C/km. Holliger et al (1978) set the minimum burial depth at 300 m (equivalent to 80 bars), while Openshaw et al (1978) estimated burial to be 3500 m (equivalent pressure 1 kilobar). Temperatures of 120 to 175°C follow for the geological environment of Oklo from these estimates. The temperature gradient must have been abrupt between the low grade ore and reaction zone as was noted by Openshaw et al (1978). For both release mechanisms, it could be assumed that the release rates were different during criticality and after the thermal period.

During the thermal phase, the elements released from the host uraninite were exposed to hot aqueous solutions convectively circulating within the reactor zones. The fluid attributed to this phase was found up to 30 m from the reactor zone; these inclusions showed a highly-variable composition. After the thermal phase, the presence of a mobile phase could be assumed as indicated by continuous migration of lead out of the reactor zone throughout the history of Oklo. Migration over distances up to 15 m were traced for Ru, ^{99}Tc and Mo. This was an unexpected behaviour as these multivalent elements are insoluble under the reducing conditions that prevailed in the geologic environment of Oklo. In evaluating migration, an attempt was made to consider the effect of chemical speciation, the presence of complexing agents, ionic strength of the solution, temperature and pressure conditions, thermodynamical stability of the species, variation of Eh, pH and fluid flow rate.

However, the conditions governing migration, with the exception of the geochemical conditions necessary for preservation of the uraninite, did not influence the release rates from the uraninite. Thus, for elements contained in the UO_2 lattice and in solid solution in the uraninite (Pd, the light REE, Th, Pu, Am, Cm), the thermodynamic conditions outside these grains were of no consequence.

The four reactor zones - No. 1, 2, 3/4 and 5/6 - known at the time of the second IAEA meeting in Paris, (1978) contained 8×10^8g uranium. About 6×10^6g ^{235}U of this amount fissioned at Oklo releasing a total energy of about 2×10^4 MW-year if 1 MW-day energy production is assumed per gram of ^{235}U fissioned. The corresponding thermal loadings ranged according to the various reaction zones from 140 to 5 W/m^2. Thus, the energy output to which the geologic environment was subjected was in a range which is projected for a nuclear waste repository.

Important findings relevant to the disposal of irradiated nuclear fuel were as follows:

(1) The 1 to 1.5 $\times 10^6$ grams of ^{239}Pu produced in the Oklo reactors did not leave the host minerals and mostly decayed to ^{235}U in the uraninite.

(2) Despite a fission density in order of 10^{20} fissions per cm^3, no trace of metamictization of uraninite was detected. Only the recrystallization of pitchblende into uraninite occurred during criticality.

(3) The release of the fission products from the crystalline host was by solid-state diffusion.

(4) The hydrogeochemical stability of the host, rather than hydrogeologic transport, controlled the distribution of fission products at Oklo over the past two-billion years.

(5) The fission products forming either metallic inclusions (Rh, Pd) in the host UO_2, or oxides stable in the uraninite structure, (Th, Pu, RRE, Bi, Te, Y, Nb), were retained within a few microns.

Those fission products forming oxides metastable in the uraninite and which were soluble in water (Sn, Sb, Pb, Cd, Rb, Cs, Sr, Ba, Mo) partly migrated.

Volatile and gaseous compounds (Kr, Xe, I) escaped almost completely.

Except for a few elements such as lead, the time of release of fissiogenic elements from the irradiated uraninite lasted only for the duration of the nuclear reaction. The time of active migration was associated with the duration of the thermal period which caused the convection of hot aqueous fluids present in the ore body.

Thermodynamic stability evaluations were used in order to determine the kind of solid compounds formed by fission products, the relative stability of the relevant minerals and the likelihood of their formation, the nature and the activity of the soluble species in equilibrium with the stable solid phase, as well as the propensity for complexation with ions in solution. This approach, however, had limitations because of deficiencies and uncertainties in relevant thermodynamic data and insufficient knowledge of chemical reactions occurring during criticality. Attempts to explain the observed migration due to the temperature dependence of solubility and changes in redox conditions due to radiolysis were more successful.

4. RECOMMENDATIONS

The Oklo natural reactors represent a high-temperature nuclear waste repository. The findings are useful mainly for the testing of assumptions, theoretical approaches and long-term predictions concerning:

- the optimum geochemical conditions for man-made nuclear waste repositories;
- the stability of mineral assemblages and barriers;
- the validity of thermodynamic evaluations;
- the behaviour of elements not occurring naturally;
- the limitations imposed on a repository due to temperature, radiation damage and radiolysis effects.

The interpretation of these factors, however, will require the evaluation of the thermo- hydrologic- chemical processes for the dynamics and distribution of the fluid convection, along with the associated mass transfer of elements. Modelling based on solution equilibrium calculations considering speciation should in this respect prove to be a better approach than pH-Eh considerations.

The findings from Oklo could be rendered more directly applicable to nuclear waste problems, if the specific results from Oklo were generalized and placed into a hydrogeologic perspective. In this respect, the study of other natural reactors is essential for generalized conclusions. Although the world-wide search was unsuccessful, there were additional reactor zones discovered at Oklo since 1978. Reactor zones, numbers 7, 8 and 9 were uncovered and from borehole cores four additional places of nuclear reaction were identified. Zones number 10 and 11 are at Oklo and numbers 12 and 13 at Okelobondo, approximately 1.5 km south of Oklo (private communication of F. Gauthier-Lafaye and F. Weber, University of Strassbourg). Of these new reactors, reactor zone number 10 showed geochemical features differing substantially from those of the other Oklo reactors. The mineral assemblage in this reactor was unique and suggested temperatures as low as 100 to 120°C during the nuclear phase while temperatures in

the other reactors were around 300 to 450°C. The investigation of reactor number 10 could provide the necessary variation of parameters required for generalized conclusions. A study comparing features of this low-temperature reactor with those of high-temperature reactors is, therefore, essential.

A research project with this objective would have to aim at reconstructing the flow regimes during nuclear and post-nuclear phases of Oklo. The approach proposed here is to study the hydrogen and oxygen isotopes in both types of reactors. The movement and origin of fluids which interacted with the Oklo reactors would be derived from the mineral $^{2}H/^{1}H$ and $^{18}O/^{16}O$ ratios, $R_{isotope}$. The temperatures would be estimated from the oxygen isotope data. The environmental isotope ratios are usually expressed as the deviations $\delta\,^{2}H$ and $\delta\,^{18}O$ in per mil (°/oo) relative to Standard Mean Ocean Water (SMOW)*. Because of slight difference in vapour pressures of hydrogen and oxygen isotopes, characteristic isotope fractionations take place in water during evaporation, condensation and chemical reactions (and other processes).

According to their fractionation history, the main terrestrial water types possess characteristic $\delta\,^{2}H$ and $\delta\,^{18}O$ concentrations which make it possible to determine the source environment and mixing patterns of the water. Hydrogen and oxygen are present in all terrestrial water types as well as in many rock-forming minerals. The $\delta\,^{2}H$ and $\delta\,^{18}O$ values of these minerals indicate the isotopic composition of the fluids involved in their formation. Since both chemical precipitation and isotope fractionation are temperature-dependent processes, the isotopic composition is also temperature dependent. The difference of $\delta\,^{18}O$ values among co-existing minerals, in accordance with the individual mineral-water fractionation equations (Taylor 1974, 1979, Clayton 1972 and Friedman 1977), is representative of the fluid temperature during mineral formation. Isotope concordancy among three co-existing minerals is required for reliable temperature estimates. In addition, one has to account for possible changes in isotope composition after mineral formation due to exchange reactions with fluids of different origins.

For the approach described above, the following strategy is recommended:

The spatial distribution of environmental isotopes in the reactor cores, inner and outer aureoles, as well as in the unaffected rock, will be established. The temperature of the environment in which the minerals characteristic for each zone were formed will be estimated from the oxygen isotope exchange equilibria among co-existing minerals. This will corroborate the temperatures derived from fluid inclusions. The existence of equilibrium/disequilibrium conditions regarding environmental isotopes along the paleo-pathways of flow will be established and the isotope composition of fluids responsible for mineral formation along these pathways derived. The information acquired will be synthesized into a model describing the hydrogeological evolution of the Oklo site during the nuclear, post-nuclear thermal, diagenetic and post-diagenetic phases.

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* δ_i°/oo = $[(R_i - R_{SMOW})/R_{SMOW}] \times 1000$

The rationale underlying this strategy is the following: The spatial survey of isotope characteristics would be the basis for solving the hydrogeological relationship between the reaction zones and confining sandstone. The study of the following minerals promises conclusive results:

Quartz, Fe-Chlorite in the outer aureol
Mg-Chlorite in the inner aureol
Hematite, Fe-Chlorite in the reactor core

The core of the low-temperature reactor number 10 contains in addition to uraninite quartz, apetite, calcite, di- and trivalent iron minerals and organic carbon.

Probably the most significant difference between the high- and low-temperature reactors is the presence of quartz in the core of the low-temperature reactor. The comparison of isotope characteristics of this reactor quartz with the quartz of the outer aureoles of the high-temperature reactors and with the quartz of the confining sandstone would illuminate the origin of the primary fluid in the Francevillian formation, moderator fluid and the post-nuclear hydrothermal solutions. Quartz is resistant to oxygen exchange with water at temperatures below 300°C and therefore the reactor quartz can be expected to have sustained the isotopic imprint of the fluid of the original reactor environment. The quartz of the aureoles probably has the isotope characteristics of the hydrothermal solutions which carried it until deposition. The quartz in the sandstone confining the high-temperature reactors is likely to have suffered an isotopic shift from the original content due to exchange with the hydrothermal fluids. Complications might arise from varying salinity of these fluids which affects the $^{18}O/^{16}O$ fractionation.

The ^{18}O of the calcite would provide a good corroboration of temperatures reached in reactor number 10.

The hydrogeochemical interpretation of isotope characteristics of chlorite will require additional considerations as the $^{2}H/^{1}H$ fractionation is affected by the Fe/Mg ratio of the mineral.

The intercomparison of the hydrogeological conditions of the high- and low-temperature reactors during the post-nuclear phase would be possible due to the presence of hematite in both reactor types. The environmental isotope composition of hematite was probably determined by fluids of lower temperatures than those convecting in the high-temperature reactors during the nuclear phase. In the low-temperature reactor number 10, the environmental isotopic composition of hematite overlaps with the thermal fields of both nuclear and post-nuclear temperatures. The changing conditions could have resulted in variation of the isotope exchange rate and consequently various stages of isotopic equilibrium could have been retained here. However, in order to attribute the hematite development to specific phases of hydrogeological evolution of the site, laboratory calibration of hematite-water environmental isotope fractionation would be required, as the relationship is not known for low temperatures.

Illite is present in the reactor cores, as well as in the aureoles. The $\delta\,^{2}H$ and $\delta\,^{18}O$ of clay minerals can be expected to have retained the characteristics of the ambient water of their formation. The isotope characteristics of the post-thermal phase fluids can be expected to be reflected in the clay minerals.

The study of environmental isotope equilibrium/disequilibrium in minerals along discontinuities would be used in combination with Weber and Gauthier-Lafaye's tectonic and kinematic analysis to identify the pathways of fluid circulation. Alterations of the fluid on its way through the reactor zone should be traceable from the degree of isotopic equilibrium observed. Besides alterations, variations due to changing fluid origin in course of the diageneses, uplift, emergence above the ocean level, can be assumed to be reflected in the $\delta\,^{2}H$ and $\delta\,^{18}O$ values of some minerals; the fluids associated with the clay mineral formation, hematite precipitation or quartz deposition were probably of diverse origin. An attempt could be made to relate the origin of moderator fluid, post-nuclear thermal fluid, as well as that of the diagenetic solutions, to the principle terrestrial water types. The pathways used by fluids of different origins could also have varied. Possibly, the flow through the bulk rock diminished continuously and the fracture flow increased during the cooling-down phase and commencement of the diageneses.

Eventually, the deep circulation regime changed due to the general uplift of the site into a shallow ground water system with normal temperatures. Although most of the alterations at Oklo occurred during the nuclear and thermal phases, the post-thermal evolution, which lasted approximately 2000 times longer than the nuclear phase, would require investigation in order to separate the effects of processes relevant for a nuclear waste repository.

The expected benefit from the investigation of the described phenomena for the Canadian Nuclear Waste Management Program would be the identification of the long-term chemical and physical changes of the ground water associated with uploading and later transition from thermal to the post-thermal phase of the repository. Environmental isotope studies of the fracture infilling minerals carried out presently (Kerrich, 1984) are very useful for identification of the hydrogeological role of fractures in plutonic rocks. They deal, however, with fractures development during the cooling-down of magmatic intrusions and with the subsequent hydrogeological activity of these fractures. The question of isotope hydrogeochemical changes of the ground water entering and leaving a nuclear repository, which acts simultaneously as a time-dependent heat, radiation and radionuclide source, remains unanswered. The proposed study of the geological reactors at Oklo would adequately address these unexplored issues.

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